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HFIP-promoted substitution in the ferrocene series: smooth approach towards original catalysts**

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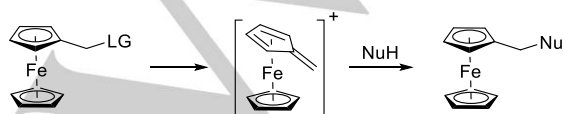
** HFIP: Hexafluoroisopropanol

Supporting information for this article is given via a link at the end of the document.

Abstract: Pseudo-benzylic substitution is an important reaction in the ferrocene series, especially to reach ligands for catalysis. Here, we described new reactions conditions, using fluorinated alcohols as both solvent and promoter, able to deliver iodoferrocene derivatives faster than using classical solvents. Various *N*, *O*, *P* and *C*-nucleophiles were found compatible with this transformation which occurs with full retention of stereochemistry. Original P,N-ligands were finally prepared by using iodine/lithium exchange-chlorophosphine trapping sequences, and their properties were evaluated in Suzuki-Miyaura and Buchwald-Hartwig coupling as well as in ketone α -arylation reaction.

Introduction

Since its discovery in 1951,^[1] ferrocene has gained a major place in chemistry.^[2] While it can be involved in many transformations, three main reactions account for its large diversity of applications: aromatic electrophilic substitution, deprotometallation-electrophilic trapping and pseudo-benzylic substitution. The latter was first reported from achiral acetoxymethylferrocene by Richards who proposed the formation of an iron-stabilized pseudo-benzylic carbocation to explain the high reaction rate.^[3] Soon after, Bacsikai and Richards found that the reaction occurs with stereoretention from chiral cyclic and acyclic ferrocenes, respectively.^[4] While the origin of the high stability of the carbocation has remained a matter of debate for years,^[5] Gleiter and Seeger validated in 1971 the structure of a fulvene bent towards the iron (Scheme 1) by using the extended Hückel model.^[6] Additional evidence of such structures was obtained in 1979 by Behrens who used X-ray diffraction analysis^[7] while detailed computational investigations were later described.^[8] Recently, Kronja revisited the early solvolysis studies, showing that the positive charge of the cation was mainly shifted to the organometallic core and that additional phenyl substituents have a limited impact on the cation stability.^[9]



Scheme 1. Pseudo-benzylic substitution in the ferrocene series. LG: leaving group, NuH: nucleophile.

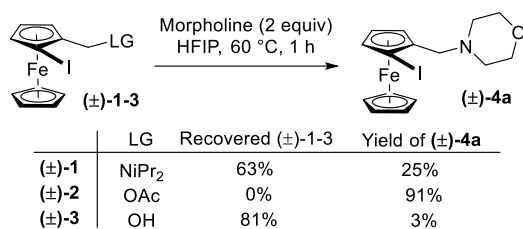
The synthetic value of this reaction was first demonstrated by Dixneuf in 1969 from achiral ferrocenemethanol derivatives, followed one year later by Ugi from chiral α -ferrocenylethylamine derivatives.^[10] The reaction was extended to other chiral substrates and nucleophiles by Dixneuf^[11] and Ugi^[12] while the use of ferrocenophane substrates was investigated with similar success by Tainturier.^[13] Over the years, the reaction was studied from a wide range of substrates, including ferrocenophanes,^[14] and various *P*-, *N*-, *O*-, *S*- and *C*-based nucleophiles,^[15] in homogeneous or biphasic systems as developed by Boev and Snegur,^[16] mainly to reach chiral ligands^[17] but also biologically active products.^[18] An important feature of this reaction is its high level of stereoretention although partial inversion can occur on specific substrates, either mono-^[14c,19] or polysubstituted^[20], which could be rationalized by following the work of Weissensteiner.^[21] Although many reaction conditions have been reported, most of them involved prolonged heating at high temperatures. Looking for smoother alternatives, Šebesta reported in 2002 the successful substitution of an acetate in aqueous media, rationalized by the formation of hydrogen bonds able to facilitate the leaving group departure.^[22] Similarly, Cozzi reported in 2007 that ferrocenyl alcohols can react with nucleophiles in such substitution “on water” at 80 °C for 24 h. Concerning alternative solvents able to establish hydrogen bonds, fluorinated alcohols emerged as promising candidates with their high hydrogen bond donating ability, increased acidity, low nucleophilicity and high dielectric constant.^[23] Therefore, they proved ideal to generate cations for both mechanistic studies^[24] and methodology development.^[25] Although fluorinated alcohols were recently used to promote reactions involving carbocations,^[26] to the best of our knowledge, only two unoptimized examples have been reported in the ferrocene series.^[27] Therefore, we decided to study the use of fluorinated alcohols to promote such pseudo-benzylic substitution.

Results and Discussion

The substrates (\pm)-**1-3** were selected to study the substitution in fluorinated alcohols (Scheme 2) as the presence of iodine would allow further functionalization. These compounds can be obtained from 2-iodo-*N,N*-diisopropylferrocenecarboxamide (see SI), accessible in both racemic and enantioenriched form.^[28] They were reacted with morpholine in an excess of hexafluoroisopropanol (HFIP) at 60 °C for 1 h. While moderate conversions were observed with *N,N*-diisopropylamino (\pm)-**1** and

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hydroxyl (**(±)-3**) as leaving groups, complete conversion was reached with the acetate (**(±)-2**), and the title product (**(±)-4a**) was isolated in a 91% yield.



Scheme 2. Evaluation of leaving groups.

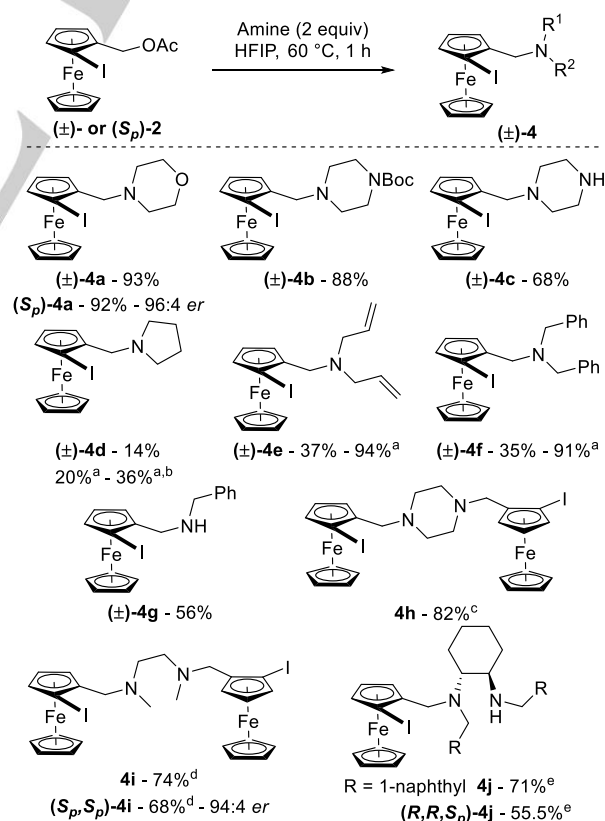
We found possible to reduce the amount of HFIP to 10 equivalents without detrimental effect (Table 1, entries 1-2) while further reduction was accompanied by a major yield drop (entry 3). The use of 1 to 4 equivalents of morpholine led to similar results (entries 2, 4-5); however, for reproducibility reasons, two equivalents of nucleophile were preferred. Conducting the reaction at lower temperature was detrimental to the yield (entries 2, 6-7) while performing the reaction at 110 °C in a sealed tube considerably fastened the reaction (entry 8). However, for safety reasons, performing reactions in regular glassware at 60 °C was preferred. Other solvents were finally evaluated. With 4 equivalents of morpholine, similar results were obtained in trifluoroethanol (TFE) and HFIP (entries 2 and 9). However, when 2 equivalents of morpholine were employed in TFE or isopropanol, a major drop of the yield was observed (entries 10-11).

Table 1. Optimization of the reaction conditions.

Entry	Solvent (equiv)	Morpholine (equiv)	T (°C)	Yield (%)
1	HFIP (30)	4	60	94
2	HFIP (10)	4	60	93
3	HFIP (5)	4	60	8
4	HFIP (10)	2	60	88
5	HFIP (10)	1	60	92
6	HFIP (10)	4	40	72
7	HFIP (10)	4	25	72
8 ^[a]	HFIP (10)	2	120	99
9	TFE (10)	4	60	86
10	TFE (10)	2	60	25
11	iPrOH (10)	2	60	Traces

[a] 10 min reaction time.

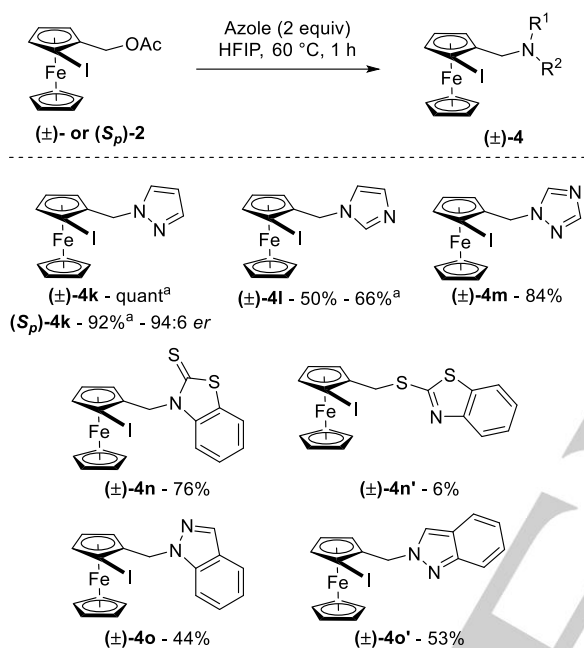
Our optimal conditions in hand, we evaluated the ability of other aliphatic amines to act as nucleophile in this HFIP-promoted substitution from both (**(±)-** and (**S_p-**)**2** (Scheme 3). As one could have expected, no erosion of the enantiomeric ratio (*er*) was observed in the reaction from (**S_p-**)**2** (*er* 96:4) to (**S_p-**)**4a**. Acting as a weakly acidic solvent, HFIP was found to tolerate *tert*-butoxycarbonyl (Boc) protecting group with compound (**(±)-4b**). Piperazine led to both the monosubstituted product (**(±)-4c** (68% yield) and disubstituted product (**(±)-4h** (24% yield)). However, moving to pyrrolidine resulted in a main drop of the yield in our standard conditions (compound (**(±)-4d**, 14% yield). This unexpected result might result from the higher nucleophilicity of pyrrolidine when compared with morpholine,^[29] leading to the formation of ammonium salts. However, further optimization using an excess of amine resulted in moderate 36% yield. Similarly, when the reaction was carried out in the presence of 2 equivalents of diallylamine or dibenzylamine, expected to be as reactive,^[29] moderate yields were recorded for the compounds (**(±)-4e** and **f** (37 and 35%, respectively). Again, using 4 equivalents of nucleophile restored high yields while benzylamine gave 56% of compound (**(±)-4g** in our standard conditions. Diamines can also be used, as shown with the compounds (**(±)-4h** and (**(±)-** or (**S_p,S_p-**)**4i**, obtained from piperazine and *N,N*-dimethylethylenediamine (DMEDA), respectively. However, for bulky diamines, we found better to react (**(±)-2** with 1.8 equivalent of both amine and HFIP, as illustrated with the compounds **4j** and (**R,R,S_p-**)**4j**. Pleasingly, it was possible to scale up the reaction to 5.0 mmol (2.3 g of compound (**(±)-4a** isolated) with similar results.



Scheme 3. Reaction between the substrates (**(±)-** and (**S_p-**)**2** and aliphatic amines. ^a 4 Equiv of amine used. ^b Addition of (**(±)-2** onto a solution of pyrrolidine in HFIP. ^c 0.5 Equiv of amine used. ^d 0.45 Equiv of amine used. ^e 1.8 Equiv of amine and 1.8 equiv of HFIP used.

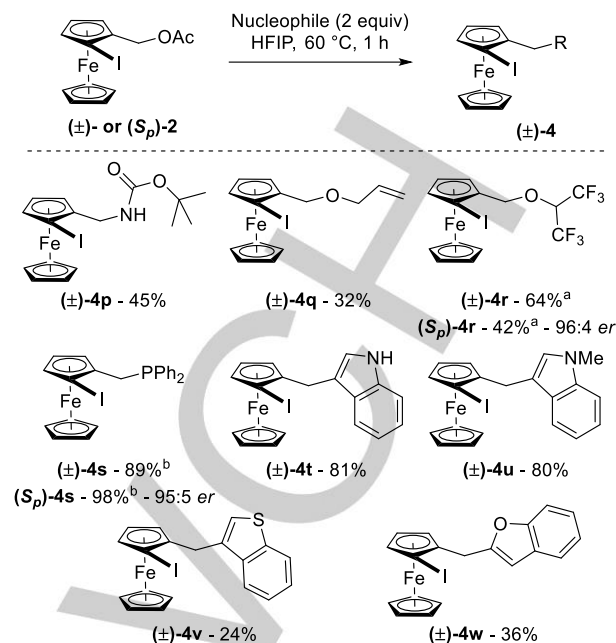
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We further engaged a few azoles in our optimized conditions (Scheme 4). While the use of pyrazole led to the compounds (\pm)-**4k** and (S_p)-**4k** in very good yields, only 50% of compound (\pm)-**4l** was isolated when imidazole was used instead. A slightly improved yield (up to 66%) was recorded when 4 equivalents of imidazole were used. The compound (\pm)-**4m** was isolated in a good 84% yield by using 1,2,4-triazole while 2-mercaptobenzothiazole conducted to the isomeric products (\pm)-**4n** and (\pm)-**4n'**. As previously observed in a related reaction,^[30] *N*-alkylation predominates over *S*-alkylation. Finally, as observed in other reaction conditions,^[31] reacting indazole with (\pm)-**2** afforded both the *N*1- and *N*2-alkylated products (\pm)-**4o** and (\pm)-**4o'** in close yields (44 and 53%, respectively).



Scheme 4. Reaction between the substrates (\pm)- and (S_p)-**2** and azoles. ^a 4 Equiv of azole used.

Then, a few other *N*-, *O*-, *P*- and *C*-nucleophiles were selected to establish the limitations of this methodology (Scheme 5). In our classical conditions, *tert*-butylcarbamate was found reactive enough to give the targeted compound (\pm)-**4p** while allylic alcohol led to the ether (\pm)-**4q** and to the unexpected product (\pm)-**4r** (32 and 24% yield, respectively). To validate the structure of the later, the substrates (\pm)- and (S_p)-**2** were heated in HFIP in the absence of any nucleophile. Full conversion was reached in only 10 min and the compounds (\pm)- and (S_p)-**4r** were isolated in moderate yields. The use of diphenylphosphine as nucleophile afforded the corresponding phosphines (\pm)- and (S_p)-**4s** in 89 and 98% yield, respectively. Indole and *N*-methylindole both afforded the expected C3-alkylated products (\pm)-**4t** and (\pm)-**4u** in similar yields (81 and 80%, respectively). However, the yield dropped when benzothiophene and benzofurane were evaluated. The only products isolated were the C3-alkylated derivative (\pm)-**4v** by starting from benzothiophene and the C2-alkylated product (\pm)-**4w** by starting from benzofuran, in line with the usual reactivity of these heterocycles.



Scheme 5. Reaction between the substrates (\pm)- and (S_p)-**2** and selected *N*-, *O*-, *P*- and *C*-nucleophiles. ^a 30 Equiv of HFIP used. ^b 4 Equiv of phosphine used.

Although a variety of nucleophiles were found to be compatible with this HFIP-promoted substitution, these reaction conditions were not suitable for some reagents such as anilines, aliphatic and aromatic thiols, pyrrole, carbazole and phenothiazine. In all these cases, various ill-defined products were formed from which we could not identify any of the desired product.

We were intrigued by the formation of the ether (\pm)-**4r** as, with the lowest Mayr's nucleophilicity parameter ($N_1 = -1.93$ for a 99:1 HFIP-water mixture), HFIP is not supposed to behave as a nucleophile.^[32] We were eager to verify if this reaction was specific to the acetate (\pm)-**2** and thus heated the amine (\pm)-**1** in pure HFIP (30 equivalents) for 14 h towards the same ether (\pm)-**4r** (Scheme 6). Although we further found that similar yields could be obtained by using only 10 equivalents of HFIP, stopping the reaction after only 1 h led to a poor conversion (a (\pm)-**1**-(\pm)-**4r** mixture was obtained in a 2.5:1 ratio).

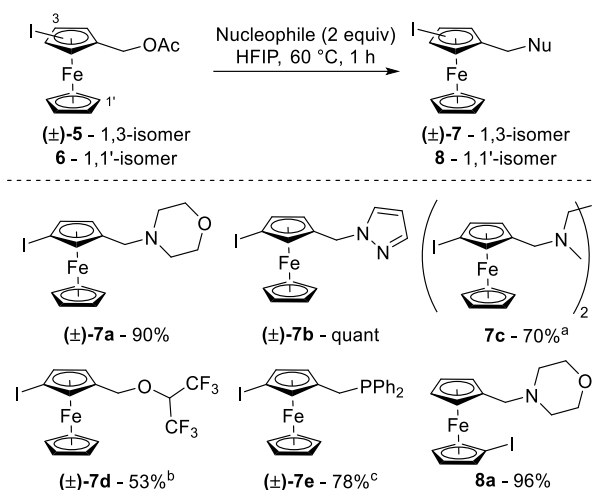


Scheme 6. Reaction between the substrates (\pm)- and (S_p)-**1** and HFIP.

As we previously reported the synthesis of the 1,1'- and 1,3-disubstituted compounds (\pm)-**5** and **6**,^[33] we were interested to evaluate the influence of the substitution pattern of ferrocene onto the reaction outcome (Scheme 7). The reaction between the 1,3-disubstituted ferrocene (\pm)-**5** and either morpholine, pyrazole or DMEDA led to the products (\pm)-**7a-c** in yields comparable to those obtained from 1-iodo-2-(acetoxymethyl)ferrocene (\pm)-**2**. However, the ether (\pm)-**7d** and the phosphine (\pm)-**7e** were obtained in slightly

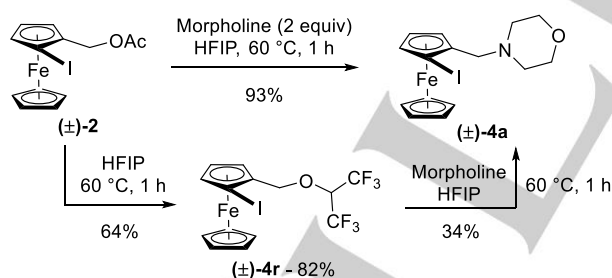
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lower yields when compared with their 1,2-disubstituted isomers. Finally, when the 1,1'-disubstituted ferrocene **6** was reacted with morpholine, the product **8a** was isolated in a 96% yield, comparable to those obtained for the 1,2- and 1,3-disubstituted isomers. Therefore, it seems that the substitution pattern of these iodoferrocenes has a limited impact onto the substitution outcome.



Scheme 7. Reaction between the substrates (\pm)-**5** and **6** and various nucleophiles. ^a 0.45 Equiv of amine used. ^b 30 Equiv of HFIP used. ^c 4 Equiv of phosphine used.

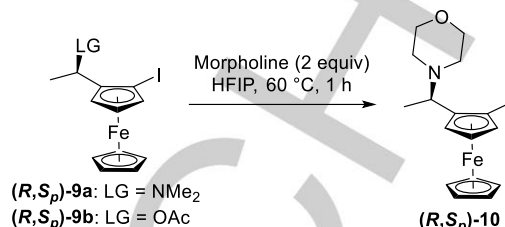
Since the ether (\pm)-**4r** can be formed in this HFIP-promoted substitution, its role as a potential intermediate raised. Therefore, the reaction between (\pm)-**4r** and morpholine (2 equiv) in HFIP was attempted at 60 °C for 1 h (Scheme 8, bottom). However, the title product (\pm)-**4a** was only isolated in a low 34% yield. Therefore, considering the low 22% overall yield to reach (\pm)-**4a** through the ether (\pm)-**4r**, its role as the main intermediate can be ruled out.



Scheme 8. Evaluation of compound (\pm)-**4r** as intermediate in the synthesis of (\pm)-**4a**.

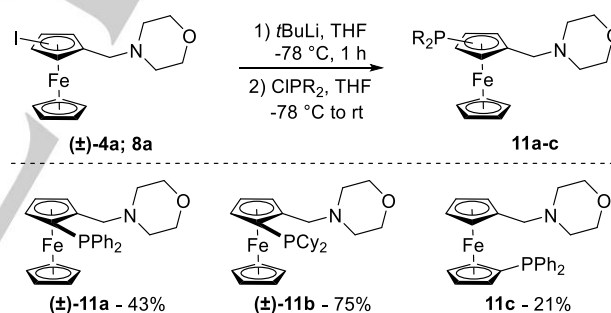
As the main application of the pseudo-benzylic substitution is to get ferrocene derivatives with both stereogenic plane and centre, derivatives of Ugi's amine were also used as substrates. Therefore, (R,S_p)-**9a** (see SI)^[34] was reacted with two equivalents of morpholine in HFIP at 60 °C (Scheme 9). However, after 1 h contact, we only recycled up to 95% of enantiopure substrate. This lack of reactivity was predictable as, except for a few azoles,^[35] replacing an amine by another one usually requires activation of the leaving group by treatment with either acetic anhydride or methyl iodide.^[15g, 36] However, the acetate (R,S_p)-**9b**

was more reactive, affording the title product (R,S_p)-**10** as a single diastereoisomer in a 78% yield with full retention of the stereochemistry, as confirmed by X-ray diffraction analysis (see SI).



Scheme 9. Reaction between substrates (R,S_p)-**9a** and (R,S_p)-**9b** with morpholine.

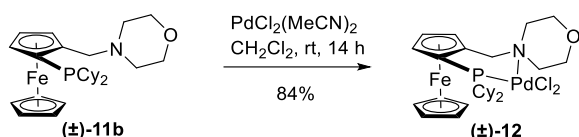
Aromatic iodides can easily be functionalized by lithium/halogen exchange, as demonstrated by Corey and Seebach^[37] toward a wide range of derivatives.^[38] Therefore, we treated the compounds (\pm)-**4a** and **8a** with a two-fold excess of *tert*-butyllithium before adding chlorodiphenyl- or chlorocyclohexylphosphine as electrophiles (Scheme 10). While the phosphines (\pm)-**11a** and (\pm)-**11b** were isolated by column chromatography in 43 and 75% yields, respectively, the compound **11c** required an intermediate protection as phosphine borane, leading to a reduced 21% overall yield.



Scheme 10. Functionalization of the iodinated ferrocenes (\pm)-**4a** and **8a**.

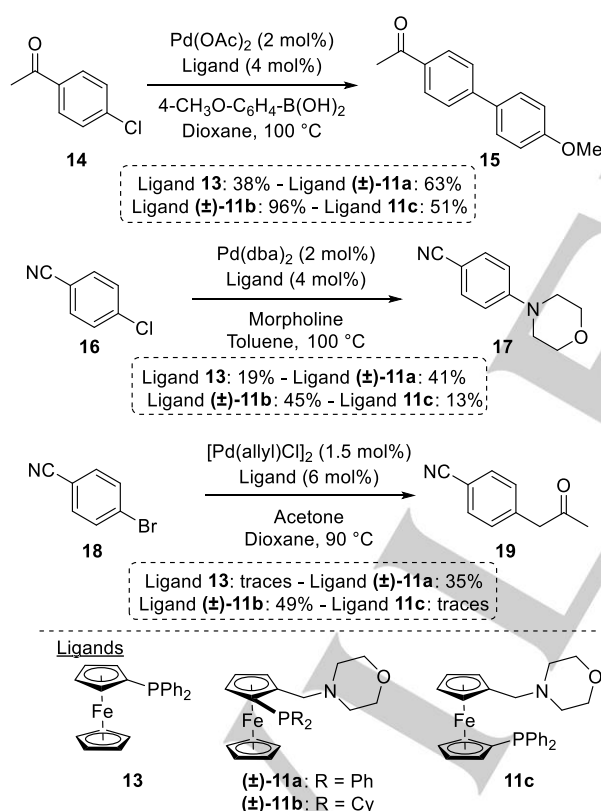
Finally, we were curious about the ligating abilities of the ferrocene phosphines **11a-c** which can behave as bidentate P,N ligands.^[39] Indeed, while related chiral ligands containing the morpholino moiety have been used in Kumada coupling and cyclobutanol opening,^[40] they have never been evaluated in other cross-couplings. As P,N ligands such as DavePhos,^[41] MorDalpos,^[42] CataCXium^[43] and an aminoferrocene derivative^[44] are efficient ligands in Suzuki-Miyaura, Buchwald-Hartwig couplings or α -arylation of ketone, we selected these reactions as benchmark tests. To evaluate the coordination ability of (\pm)-**11b**, it was first reacted with $\text{PdCl}_2(\text{MeCN})_2$ in CH_2Cl_2 at room temperature toward the complex (\pm)-**12** (Scheme 11), as demonstrated by NMR and high-resolution mass spectrometry (see SI).

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Scheme 11. Formation of the complex (±)-12.

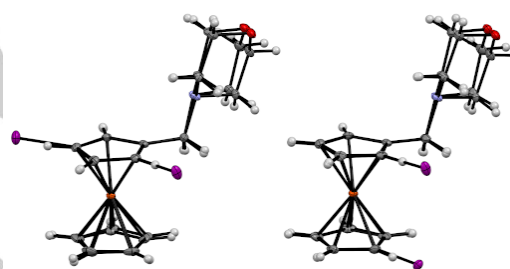
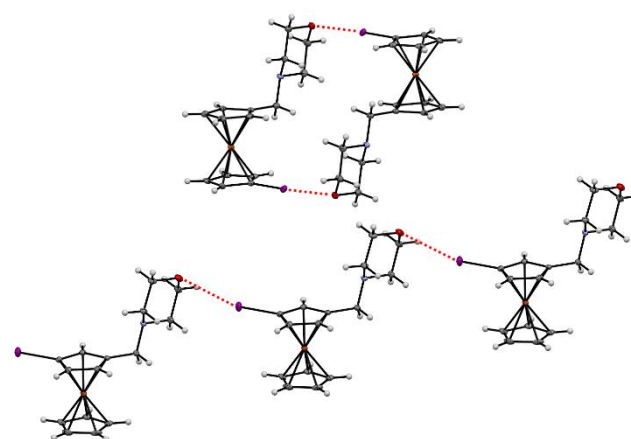
Preliminary experiments were finally performed to evaluate the ability of the phosphines **11a-c** to act as ligands in the selected reactions (Scheme 12). Furthermore, to establish whether the morpholine moiety was required, the simple (diphenylphosphino)ferrocene (**13**) was also tested. A Suzuki-Miyaura cross-coupling between 4-chloroacetophenone (**14**) and 4-methoxyphenylboronic acid in the presence of Pd(OAc)₂ was first attempted and, while all our new ligands gave better results than **13**, the best results were obtained with the bulky and electron-rich phosphine (±)-**11b**. In the Buchwald-Hartwig amination of 4-chlorobenzonitrile (**16**) with morpholine, as well as in the α-arylation of acetone with 4-bromobenzonitrile (**18**), the 1,2-disubstituted phosphines (±)-**11a,b** were the most efficient ligands, the latter being slightly better.

Scheme 12. Preliminary investigation of the use of the ligands **11a-c** and **13** in palladium-catalysed transformations.

From these unoptimized experiments, the compound (±)-**11b** appears as the most promising of the three ligands prepared. However, although none of our ligands can currently outperform other reported P,N ligands, the rapid generation of many derivatives allowed by the easy variation of the amine and

phosphine groups would facilitate the search of better ligands, possibly enantioenriched by starting from (*S_p*)-**2**.

Some of the obtained solid-state structures obtained in the course of this study deserve a few words. Indeed, we found that the geometry of the three isomers (±)-**4a**, (±)-**7a** and **8a** was not influenced by the position of iodine as indicated by the good overlay between (±)-**4a** and (±)-**7a** (RMS 0.0264 Å, Figure 1, left) and between (±)-**4a** and **8a** (RMS 0.0144 Å, Figure 1, right). However, different intramolecular interactions were observed as the 1,1'-substitution pattern of compound **8a** allows the formation of a homodimer linked by two I...O halogen bonds (Figure 2, top) while the 1,3-substitution pattern of compound (±)-**7a** favours the formations of strings of I...O halogen bonds (Figure 2, bottom). Similar halogen bonds were recently identified in the ferrocene series^[45] and result from an interaction between the lone pair of the oxygen and the σ-hole of the iodine atom.^[46] Further intermolecular interactions were also observed for the compounds (*R,S_p*)-**10** and (±)-**4n**. Indeed, for the former, we identified I...N interactions which form a zig zag bonding network (Figure 3, top) while halogen bonds^[47] between iodine and the exocyclic sulfur atom were observed for the latter (Figure 3, bottom).

Figure 1. Overlay of the compounds (±)-**4a** and (±)-**7a** (left) and (±)-**4a** and **8a** (right). Thermal ellipsoids shown at the 30% probability level.Figure 2. Halogen bond network observed for the compounds (±)-**7a** (top) and **8a** (bottom). Thermal ellipsoids shown at the 30% probability level. Selected bond lengths and angles: I...O 3.294(2) Å and C-I...O 165.26(9) ° for (±)-**7a**, I...O 3.1069(18) Å and C-I...O 176.41(7) ° for **8a**.

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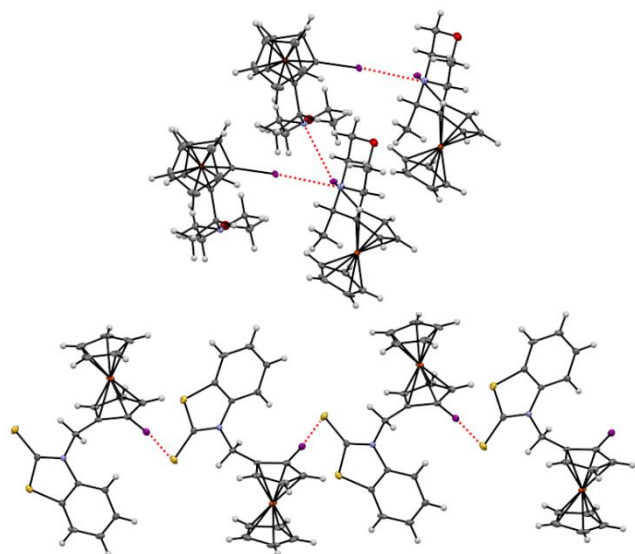


Figure 3. Halogen bond network observed for the compounds (*R,S_p*)-**10** (top) and (\pm)-**4n** (bottom). Thermal ellipsoids shown at the 30% probability level. Selected bond lengths and angles: I...N 3.225(3) Å and C-I...N 160.71(10) ° for (*R,S_p*)-**10**, I...N 3.3584(8) Å, C-I...S and C-S...I 176.34(7) ° and 83.91(9) ° for (\pm)-**4n**.

Conclusion

In conclusion, we have developed new reaction conditions, using fluorinated alcohols, to promote a pseudo-benzylic substitution in the ferrocene series. With smooth reaction conditions (moderate temperature and short reaction time), it was possible to replace an acetate by a variety of *N*, *O*, *P*, and *C* nucleophiles. The reaction occurs with a high degree of stereochemical retention for substrates having only a stereogenic plane or both stereogenic plane and centre. Furthermore, an original ferrocene substituted by a hexafluoropropoxyxymethyl group was isolated, indicating that from specific substrates and under the right reaction conditions, HFIP can behave as a nucleophile, contrary to the general thought. Three original phosphinoferrocene derivatives were finally prepared and used as ligand in cross-couplings. From this preliminary evaluation, one ligand emerged as promising for this application. As pseudo-benzylic substitution is widely used in the ferrocene series, it makes little doubt that combining these easily set-up fast reaction conditions with further functionalization will find applications, especially in the preparation of libraries of ligands for applications in catalysis.

Experimental Section

General Considerations. All nucleophilic substitutions promoted by HFIP were performed under air. Unless otherwise stated, all the other reactions were performed under an argon atmosphere with anhydrous solvents using Schlenk techniques. THF and dioxane were distilled over sodium/benzophenone, acetone was dried by prolonged contact over activated 3Å molecular sieve,^[48] toluene and dichloromethane were distilled over CaH₂. Unless otherwise stated, all reagents were used without prior purification. All organolithium reagents were titrated before use.^[49] Column chromatography separations were achieved on silica gel (40–63 μm). PE refers to petroleum ether, rt refers to room temperature (25 °C). All Thin Layer Chromatographies (TLC) were performed on aluminium backed plates pre-coated with silica gel (Merck, Silica Gel 60

F254). They were visualized by exposure to UV light. Melting points were measured on a Kofler bench. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ¹H and ¹³C{¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded either (a) on a Bruker Avance III spectrometer at 300 MHz and 75.4 MHz, respectively, or (b) Bruker Avance III HD at 400 MHz and 100 MHz, respectively, or (c) on a Bruker Avance III HD at 500 MHz and 126 MHz, respectively. ¹H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ¹³C chemical shifts are relative to the central peak of the solvent signal. Elemental analyses were performed on a Thermo Fischer 1112 HT apparatus and HRMS were recorded on a Thermo Fisher Q-Exactive mass spectrometer at the Centre Régional de Mesures Physiques de l'Ouest. The numbering used in this Experimental Section is defined in Supporting Information. (*R,R*)-(-)-Cyclohexane-1,2-diamine was prepared according to Jacobsen.^[50] (*R,R*)-*N,N'*-bis(1-naphthylmethyl)cyclohexane-1,2-diamine was prepared according to Smith.^[51]

Safety Considerations. Due to its high pyrophoric character, *n*BuLi need to be used only under inert conditions (anhydrous, nitrogen or argon atmosphere) and by people well-trained to the manipulation of reactive organometallics.

Crystallography. For (\pm)-**4a**, (\pm)-**4n**, (\pm)-**4s**, (\pm)-**4v**, (\pm)-**4w**, (\pm)-**7b**, **8a** and (\pm)-**11b**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector. For (\pm)-**7a** and (*R,S_p*)-**10**, the X-ray diffraction data were collected using APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector. The samples were studied with monochromatized Mo-K α radiation (λ = 0.71073 Å) at the temperature given in the crystal data. The structure was solved by dual-space algorithm using the *SHELXT* program,^[52] and then refined with full-matrix least-square methods based on *F*² (*SHELXL*).^[53] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by MERCURY 2020.3.0.

General procedure A: HFIP-promoted substitution. HFIP (10.0 equiv) was added to a mixture of the required substrate (1.00 equiv) and required nucleophile (2.00 equiv) and the reaction mixture was heated for 1 h at 60 °C in a pre-heated oil bath. The reaction was cooled to rt and was poured onto a NEt₃-EtOAc mixture (1:1) and volatiles were removed under vacuum to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (eluent given in product description) to give the title product.

(\pm)-1-Iodo-2-(*N*-morpholinomethyl)ferrocene ((\pm)-4a**):** By following the general procedure A from compound (\pm)-**2** (115 mg, 0.30 mmol) and morpholine (52.5 μL, 52.3 mg, 0.60 mmol) in HFIP (316 μL), (\pm)-**4a** was obtained after column chromatography (PE-EtOAc, 40:60 with 1% of NEt₃) as an orange solid (115 mg, 93%). *R_f* (eluent: PE/EtOAc 40:60, 5 drops of NEt₃) = 0.21. Mp 63–65 °C. ν_{max} (film)/cm⁻¹ 2955, 2935, 2805, 1455, 1446, 1331, 1285, 1263, 1243, 1222, 1111, 999, 918, 859, 809. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.43 (dd, *J* = 1.4, 2.0 Hz, 1H, FcCH, H5), 4.29 (dd, *J* = 1.3, 2.2 Hz, 1H, FcCH, H3), 4.21 (t, *J* = 2.5 Hz, 1H, FcCH, H4), 4.11 (s, 5H, Cp), 3.65 (t, *J* = 4.7 Hz, 4H, 2 x CH₂O), 3.47 (d, *J* = 13.3 Hz, 1H, CHH), 3.41 (d, *J* = 13.3 Hz, 1H, CHH), 2.57 (m, 2H, CH₂N), 2.40 (m, 2H, CH₂N). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ (ppm) 84.1 (FcC, C2), 75.0 (FcCH, C5), 71.7 (Cp), 69.2 (FcCH, C4), 69.1 (FcCH, C3), 67.1 (2 x CH₂O), 58.1 (CH₂), 53.3 (2 x CH₂N), 46.5 (FcC, C1). Mass: 411 [M], 325 [M-C₄H₈NO]. Anal. Calcd for C₁₅H₁₈FeINO: C, 43.83; H, 4.41; N, 3.41. Found: C, 43.75; H, 4.36; N, 3.26. **Crystal data for (\pm)-**4a**.** C₁₅H₁₈FeINO, *M* = 411.05, *T* = 150 K; orthorhombic *Pbc**a* (I.T.#61), *a* = 11.233(2), *b* = 9.5399(17), *c* = 27.474(6) Å, *V* = 2944.2(10) Å³. *Z* = 8, *d* = 1.855 g·cm⁻³, μ = 3.113 mm⁻¹. A final refinement on *F*² with 3376 unique intensities and 172 parameters converged at ωR^2 = 0.0597 (*R_f* = 0.0252) for 3055 observed reflections with *I* > 2 σ (*I*). CCDC 2090455.

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(S_p)-1-Iodo-2-(N-morpholinomethyl)ferrocene ((S_p)-4a): By following the general procedure A, starting from **(S_p)-2a** (115 mg, 0.30 mmol, 96:4 er) and morpholine (52.5 μL, 52.3 mg, 0.60 mmol) in HFIP (316 μL), the title product was obtained as an orange solid (113 mg, 92%, 96:4 er). Analytical data analogous to racemic compound. [α]_D +13.3 (c 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IA-3 column, hexane with 0.1% of diethylamine/iPrOH: 95:5, 1.0 mL·min⁻¹, 10 °C, λ = 254 nm, t (major) = 6.94 min, t (minor) = 7.33 min.

(±)-1-Iodo-2-(N-tert-butoxycarbonyl-N-piperazino)methylferrocene ((±)-4b): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol) and N-tert-butoxycarbonylpiperazine (149 mg, 0.80 mmol) in HFIP (421 μL), **(±)-4b** was obtained after column chromatography (PE-EtOAc, 80:20 to 60:40 with 1% of NEt₃) as an orange solid (180 mg, 88%). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.28. Mp 103-104 °C. ν_{max} (film)/cm⁻¹ 3008, 2967, 2929, 2808, 1683, 1454, 1420, 1364, 1296, 1269, 1229, 1171, 1160, 1144, 1117, 1000, 947, 866, 822, 810, 764. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.43 (s, 1H, FcCH, H5), 4.28 (s, 1H, FcCH, H3), 4.22 (t, J = 2.1 Hz, 1H, FcCH, H4), 4.11 (s, 5H, Cp), 3.50 (d, J = 13.3 Hz, 1H, CHH), 3.44 (d, J = 13.3 Hz, 1H, CHH), 3.39-3.36 (m, 4H, 2 x CH₂NC(O)), 2.47-2.45 (m, 2H, CH₂N), 2.35-2.33 (m, 2H, CH₂N), 1.43 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 154.8 (C=O), 84.1 (FcC, C2), 79.7 (C(CH₃)₃), 75.0 (FcCH, C5), 71.7 (Cp), 69.3 (FcCH, C4), 69.1 (FcCH, C3), 57.7 (CH₂), 52.5 (2 x CH₂N), 46.5 (FcC, C1), 44.0 (CH₂NC(O)), 43.3 (CH₂NC(O)), 28.6 (C(CH₃)₃). Anal. Calcd for C₂₀H₂₇FeIN₂O₂: C, 47.08; H, 5.33; N, 5.49. Found: C, 47.06; H, 5.20; N, 5.22.

(±)-1-Iodo-2-(N-piperazino)methylferrocene ((±)-4c): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol) and piperazine (68.9 mg, 0.80 mmol) in HFIP (421 μL), **(±)-4c** was obtained after column chromatography (PE-EtOAc, 90:10 with 2% of NEt₃) as an orange oil (112 mg, 68%). R_f (eluent: EtOAc) = 0.15. ν_{max} (film)/cm⁻¹ 3365, 2922, 2810, 1637, 1563, 1454, 1409, 1368, 1329, 1298, 1134, 1105, 998, 806. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.74 (br s, 1H, NH), 4.40 (s, 1H, FcCH, H5), 4.25 (s, 1H, FcCH, H3), 4.19 (s, 1H, FcCH, H4), 4.09 (s, 5H, Cp), 3.44 (s, 2H, CH₂), 2.90 (br s, 4H, 2 x CH₂NH), 2.56 (br s, 2H, CH₂N), 2.46 (br s, 2H, CH₂N). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 84.0 (FcC, C2), 75.0 (FcCH, C5), 71.7 (Cp), 69.2 (FcCH, C4), 69.1 (FcCH, C3), 57.9 (CH₂), 52.5 (2 x CH₂N), 46.4 (FcC, C1), 45.2 (2 x CH₂NH). Anal. Calcd for C₁₅H₁₉FeIN₂: C, 43.93; H, 4.67; N, 6.83. Found: C, 43.82; H, 4.51; N, 6.76. Compound **(±)-4h** was also isolated as an orange solid (36 mg, 24%).

(±)-1-Iodo-2-(N-pyrrolidinomethyl)ferrocene ((±)-4d): Compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) was added in four portions to a solution of pyrrolidine (133 μL, 114 mg, 1.6 mmol, 4.00 equiv) in HFIP (421 μL, 672 mg, 4.00 mmol, 10.0 equiv) at rt. After addition the reaction mixture was heated for 1 h at 60 °C in a pre-heated oil bath. The reaction was cooled to rt and was poured onto a NEt₃-EtOAc mixture (1:1, 2 mL) and volatiles were removed under vacuum to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (40:60 to 30:70 with 2% of NEt₃) to give the title product as an orange oil (57 mg, 36%). R_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.55. ν_{max} (film)/cm⁻¹ 3093, 2961, 2925, 2780, 1673, 1457, 1374, 1346, 1314, 1258, 1236, 1105, 1059, 1028, 999, 875, 818, 804. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.41 (dd, J = 1.5, 2.0 Hz, 1H, FcCH, H5), 4.32 (dd, J = 1.5, 2.3 Hz, 1H, FcCH, H3), 4.20 (t, J = 2.5 Hz, 1H, FcCH, H4), 4.11 (s, 5H, Cp), 3.62 (d, J = 13.2 Hz, 1H, CHH), 3.47 (d, J = 13.2 Hz, 1H, CHH), 2.68-2.56 (m, 2H, CH₂N), 2.52-2.45 (m, 2H, CH₂N), 1.77-1.69 (m, 4H, 2 x CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 85.8 (FcC, C2), 74.7 (FcCH, C5), 71.7 (Cp), 69.1 (FcCH, C4), 68.7 (FcCH, C3), 54.8 (CH₂), 53.9 (2 x CH₂N), 46.1 (FcC, C1), 23.6 (2 x CH₂). Anal. Calcd for C₁₅H₁₈FeIN: C, 45.60; H, 4.59; N, 3.55. Found: C, 45.73; H, 4.70; N, 3.72.

(±)-1-Iodo-2-(N,N-diallylaminomethyl)ferrocene ((±)-4e): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol) and diallylamine (198 μL, 155 mg, 1.60 mmol) in HFIP (421 μL), **(±)-4e** was obtained after column chromatography (PE-EtOAc, 95:5 with 2% of NEt₃)

as an orange oil (159 mg, 94%). R_f (eluent: PE/EtOAc 95:5, 5 drops of NEt₃) = 0.54. ν_{max} (film)/cm⁻¹ 3075, 2918, 2800, 1675, 1641, 1445, 1416, 1372, 1350, 1254, 1105, 997, 975, 915, 820, 806, 749. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.87 (ddt, J = 6.2, 10.2, 17.1 Hz, 2H, 2 x CH=CHH, 5.20 (d, J = 17.1 Hz, 2H, 2 x CH=CHH), 5.14 (d, J = 10.2 Hz, 2H, 2 x CH=CHH), 4.41 (s, 1H, FcCH, H5), 4.30 (s, 1H, FcCH, H3), 4.19 (s, 1H, FcCH, H4), 4.09 (s, 5H, Cp), 3.55 (d, J = 13.7 Hz, 1H, CHH), 3.42 (d, J = 13.7 Hz, 1H, CHH), 3.11 (dd, J = 6.2, 14.0 Hz, 2H, 2 x CHH), 3.05 (dd, J = 6.2, 14.0 Hz, 2H, 2 x CHH). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 136.3 (CH=CHH), 117.4 (CH=CHH), 85.9 (FcC, C2), 74.8 (FcCH, C5), 71.7 (Cp), 69.1 (FcCH, C3), 68.9 (FcCH, C4), 56.4 (2 x CH₂), 52.9 (CH₂), 46.0 (FcC, C1). Anal. Calcd for C₁₇H₂₀FeIN: C, 48.49; H, 4.79; N, 3.33. Found: C, 43.40; H, 4.73; N, 3.25.

(±)-1-Iodo-2-(N,N-dibenzylaminomethyl)ferrocene ((±)-4f): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol) and dibenzylamine (307 μL, 316 mg, 1.60 mmol) in HFIP (421 μL), **(±)-4f** was obtained after column chromatography (PE-EtOAc, 95:5 with 2% of NEt₃) as an orange oil (200 mg, 91%). R_f (eluent: PE/EtOAc 95:5, 5 drops of NEt₃) = 0.84. ν_{max} (film)/cm⁻¹ 3024, 2791, 1493, 1451, 1368, 1229, 1105, 1027, 1000, 973, 957, 821, 806, 732, 695. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.40 (d, J = 7.4 Hz, 4H, ArCH, 4 x H₂'), 7.32 (t, J = 7.4 Hz, 4H, ArCH, 4 x H₃'), 7.24 (t, J = 7.4 Hz, 2H, ArCH, 2 x H₄'), 4.41 (dd, J = 1.4, 2.3 Hz, 1H, FcCH, H5), 4.36 (dd, J = 1.4, 2.3 Hz, 1H, FcCH, H3), 4.18 (t, J = 2.4 Hz, 1H, FcCH, H4), 3.60 (d, J = 13.7 Hz, 2H, 2 x CHHPh), 3.59 (d, J = 13.8 Hz, 1H, CHH), 3.54 (d, J = 13.7 Hz, 2H, 2 x CHHPh), 3.45 (d, J = 13.8 Hz, 1H, CHH). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 139.9 (ArC, 2 x C¹'), 128.9 (ArCH, 4 x C²'), 128.3 (ArCH, 4 x C³'), 126.9 (ArCH, 2 x C⁴'), 86.1 (FcC, C2), 74.7 (FcCH, C5), 71.7 (Cp), 69.2 (FcCH, C3), 68.7 (FcCH, C4), 57.9 (2 x CH₂Ph), 53.4 (CH₂), 45.6 (FcC, C1). Anal. Calcd for C₂₅H₂₄FeIN: C, 57.61; H, 4.64; N, 2.69. Found: C, 57.71; H, 4.60; N, 2.66.

(±)-1-Iodo-2-(N-benzylaminomethyl)ferrocene ((±)-4g): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol) and benzylamine (87.4 μL, 85.7 mg, 0.80 mmol) in HFIP (421 μL), **(±)-4g** was obtained after column chromatography (PE-EtOAc, 90:10 with 1% of NEt₃) as an orange solid (97 mg, 56%). R_f (eluent: PE/EtOAc 40:60, 5 drops of NEt₃) = 0.74. Mp 66-67 °C. ν_{max} (film)/cm⁻¹ 3084, 3026, 2939, 2917, 2833, 1493, 1452, 1407, 1365, 1105, 1064, 1052, 1026, 997, 972, 957, 824, 811, 800, 731. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.36-7.32 (m, 4H, ArCH, 2 x H₂' and 2 x H₃'), 7.27-7.25 (m, 1H, ArCH, H₄'), 4.42 (s, 1H, FcCH, H5), 4.28 (s, 1H, FcCH, H3), 4.19 (s, 1H, FcCH, H4), 4.11 (s, 5H, Cp), 3.84 (d, J = 13.3 Hz, 1H, CHHPh), 3.79 (d, J = 13.3 Hz, 1H, CHHPh), 3.70 (d, J = 13.4 Hz, 1H, CHHN), 3.53 (d, J = 13.4 Hz, 1H, CHHN). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 140.4 (ArC, C¹'), 128.5 (ArCH, 2 x C²'), 128.3 (ArCH, 2 x C³'), 127.1 (ArCH, C⁴'), 87.5 (FcC, C2), 74.7 (FcCH, C5), 71.6 (Cp), 68.7 (FcCH, C4), 68.1 (FcCH, C3), 53.3 (CH₂Ph), 48.7 (CH₂N); 44.8 (FcC, C1). Anal. Calcd for C₁₈H₁₈FeIN: C, 50.15; H, 4.21; N, 3.25. Found: C, 50.11; H, 4.37; N, 3.36.

N,N-bis-(2-Iodoferrocenylmethyl)piperazine (4h): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and piperazine (17.3 mg, 0.20 mmol, 0.50 equiv) in HFIP (421 μL), **(±)-4h** was obtained after column chromatography (PE-EtOAc, 50:50 to 30:70 with 2% of NEt₃) as an orange solid (121 mg, 82%). R_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.55. Mp < 50 °C. ν_{max} (film)/cm⁻¹ 3092, 2929, 2805, 2767, 1645, 1453, 1368, 1328, 1285, 1151, 1132, 1105, 1001, 944, 806, 748. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.39 (m, 2H, FcCH, 2 x H5), 4.27 (m, 2H, FcCH, 2 x H3), 4.18 (m, 2H, FcCH, 2 x H4), 4.09 (s, 10H, 2 x Cp), 3.48 (d, J = 13.2 Hz, 2H, 2 x CHH), 3.39 (d, J = 13.2 Hz, 2H, 2 x CHH), 2.53 (br s, 4H, 2 x CH₂N), 2.42 (br m, 4H, 2 x CH₂N). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 84.4 (FcC, 2 x C2), 74.9 (FcCH, 2 x C5), 71.7 (2 x Cp), 69.2 (FcCH, 2 x C4), 69.1 (FcCH, 2 x C3), 57.5 (2 x CH₂), 52.6 (4 x CH₂N), 46.6 (FcC, 2 x C1). Anal. Calcd for C₂₆H₂₈Fe₂I₂N₂: C, 42.54; H, 3.85; N, 3.82. Found: C, 42.60; H, 3.82; N, 3.90.

N,N-Dimethyl-N,N-bis-(2-iodoferrocenylmethyl)ethylenediamine ((±)-4i): By following the general procedure A from compound **(±)-2** (169

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mg, 0.44 mmol, 2.20 equiv) and *N,N*-dimethylethylenediamine (21.5 μ L, 17.6 mg, 0.20 mmol, 1.00 equiv) in HFIP (210 μ L), (**\pm**)-**4i** was obtained after column chromatography (PE-EtOAc, 30:70 to 10:90 with 2% of NEt₃) as an orange oil (109 mg, 74%). R_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.13. ν_{max} (film)/cm⁻¹ 3093, 2939, 2778, 1452, 1411, 1371, 1233, 1217, 1105, 1019, 1000, 821, 807, 747. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.41 (s, 2H, FcCH, 2 x H5), 4.28 (s, 2H, FcCH, 2 x H3), 4.20 (s, 2H, FcCH, 2 x H4), 4.10 (s, 10H, 2 x Cp), 3.44 (m, 4H, 2 x CH₂-Fc), 2.51 (s, 4H, 2 x CH₂-N), 2.20 (s, 6H, 2 x CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 85.0 (FcC, 2 x C2), 74.9 (FcCH, 2 x C5), 71.7 (2 x Cp), 69.2 (FcCH, 2 x C4), 69.1 (FcCH, 2 x C3), 57.2 (CH₂-Fc), 57.0 (CH₂-Fc), 54.9 (CH₂-N), 54.8 (CH₂-N), 46.7 (FcC, 2 x C1), 42.5 (2 x CH₃). Anal. Calcd for C₂₆H₃₀FeI₂N₂: C, 45.91; H, 4.45; N, 4.12. Found: C, 46.04; H, 4.56; N, 4.20.

(S_p,S_p)-N,N'-Dimethyl-N,N'-bis(2-

iodoferrocenylmethyl)ethylenediamine ((S_p,S_p)-4i**):** By following the general procedure A from compound (**S_p**)-**2** (169 mg, 0.44 mmol, 2.20 equiv) and *N,N*-dimethylethylenediamine (21.5 μ L, 17.6 mg, 0.20 mmol, 1.00 equiv) in HFIP (210 μ L), (**S_p,S_p**)-**4i** was obtained after column chromatography (PE-EtOAc, 30:70 to 10:90 with 2% of NEt₃) as an orange oil (100 mg, 68%, 94:6 er). Analytical data analogous to racemic compound. [α]_D +33.3 (c 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IA-3 column, hexane with 0.1% of diethylamine/iPrOH: 97:3, 0.8 mL·min⁻¹, 5 °C, λ = 254 nm, t (major) = 15.85 min, t (minor) = 14.31 min.

(1R,2R)-N,N'-Bis(1-naphthylmethyl)-N-(\pm)-2-

iodoferrocenylmethyl)cyclohexane-1,2-diamine ((\pm)-4j**):** HFIP (42.0 μ L, 67.2 mg, 0.40 mmol, 1.80 equiv) was added to a mixture of compound (**\pm**)-**2** (38.4 mg, 0.10 mmol, 1.00 equiv) and (*R,R*)-*N,N'*-bis(1-naphthylmethyl)cyclohexane-1,2-diamine (158 mg, 0.40 mmol, 1.80 equiv) in a dry tube under argon and the reaction mixture was heated overnight at 60 °C (oil bath, external temperature). The reaction mixture was cooled to rt and HFIP (42.0 μ L, 67.2 mg, 0.40 mmol, 1.80 equiv) was added before the reaction mixture was heated for 4 more hours at 60 °C. The reaction mixture was cooled to rt, a buffered aqueous solution (5 mL, pH 7) was added and the reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE/EtOAc (10:1) with 2% of NEt₃ to give the title product as an orange oil (51.0 mg, 71%). Analytical data in agreement with enantioenriched compound.

(1R,2R)-N,N'-Bis(1-naphthylmethyl)-N-(S_p)-2-

iodoferrocenylmethyl)cyclohexane-1,2-diamine ((R,R,S_p)-4j**):** By following a similar protocol, starting from (**S_p**)-**2** (38.4 mg, 0.10 mmol, 1.00 equiv, 96:4 er) and (*R,R*)-*N,N'*-bis(1-naphthylmethyl)cyclohexane-1,2-diamine (158 mg, 0.40 mmol, 4.00 equiv), the title product was obtained as an orange oil (40.0 mg, 55.5%). Attempts to determine the enantiomeric ratio by chiral HPLC failed to provide any separation. [α]_D -39.8 (c 0.01 in CHCl₃). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.66. ν_{max} (film)/cm⁻¹ 2929, 2855, 1597, 1510, 1449, 1216, 1106, 1001, 791, 773, 754. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.91 (d, *J* = 8.6 Hz, 1H, ArCH, H27), 7.81 (d, *J* = 5.3 Hz, 1H, ArCH, H14 or H16 or H21), 7.80 (d, *J* = 7.1 Hz, 1H, ArCH, H14 or H16 or H21), 7.75-7.72 (m, 2H, 2 x ArCH, H24 and H14 or H21), 7.64 (d, *J* = 8.2 Hz, 1H, ArCH, H11), 7.44-7.39 (m, 3H, 3 x ArCH, H11 and H20 and H22), 7.37-7.31 (m, 2H, 2 x ArCH, H25 and H14 or H21), 7.22 (t, *J* = 7.5 Hz, 1H, ArCH, H10), 7.16 (dt, *J* = 1.0, 7.6 Hz, 1H, ArCH, H26), 6.88 (br s, 1H, ArCH, H9), 4.33 (s, 1H, FcCH, H32), 4.27 (d, *J* = 13.3 Hz, 1H, CHH, H18), 3.99 (s, 7H, Cp and FcCH, H35 and H33 and H34), 3.96 (d, *J* = 13.1 Hz, 1H, CHH, H7), 3.88 (d, *J* = 13.3 Hz, 1H, CHH, H18), 3.78 (d, *J* = 13.6 Hz, 1H, CHH, H29), 3.52 (d, *J* = 13.6 Hz, 1H, CHH, H29), 3.48 (d, *J* = 13.1 Hz, 1H, CHH, H7), 2.85 (s, 1H, NH), 2.76 (t, *J* = 9.5 Hz, 1H, CHN, H4), 2.55 (s, 1H, CHN, H6), 2.18 (d, *J* = 11.9 Hz, 1H, C_aHH, H5), 2.09 (d, *J* = 12.5 Hz, 1H, C_bHH, H2), 1.91 (dd, *J* = 2.9, 6.4 Hz, 1H, C_aHH, H3), 1.73 (dd, *J* = 2.1, 5.9 Hz, 1H, C_aHH, H4), 1.62 (dq, *J* = 3.2, 12.0 Hz, 1H, C_bHH, H2), 1.33-1.25 (m, 2H, C_cHH, C_dHH, H3 and H4), 1.04

(dq, *J* = 2.1, 10.9 Hz, 1H, C_aHH, H5). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 136.7 (ArC, C8), 135.6 (ArC, C19), 134.0 (ArC, C12), 133.5 (ArC, C23), 132.6 (ArC, C28), 131.6 (ArC, C17), 128.5 (ArCH, 128.4 (ArCH, 128.1 (ArCH, C24), 127.8 (ArCH, C20), 126.6 (ArCH, C11), 126.0 (ArCH, C26), 125.6 (3 x ArCH), 125.2 (ArCH), 125.1 (ArCH), 125.0 (ArCH, C27), 124.3 (ArCH, C9), 123.5 (ArCH), 86.6 (FcC, C30), 75.0 (FcCH, C32), 71.7 (Cp), 70.0 (FcCH, C34), 69.1 (FcCH, C33), 64.0 (CHN, C1), 58.5 (CHN, C6), 53.2 (CH₂, C18), 49.5 (CH₂, C29), 47.6 (CH₂, C7), 45.4 (FcC, C31), 32.1 (C_aH₂, C5), 26.0 (C_cH₂, C3), 24.9 (C_dH₂, C4), 22.8 (C_bH₂, C2). Recovery of the remaining (*R,R*)-*N,N'*-bis(1-naphthylmethyl)cyclohexane-1,2-diamine by column chromatography afforded 69.0 mg of pure product.

(\pm)-1-Iodo-2-(N-pyrazolinomethyl)ferrocene ((\pm)-4k**):** By following the general procedure A from compound (**\pm**)-**2** (23 mg, 0.06 mmol, 1.00 equiv) and pyrazole (16.3 mg, 0.24 mmol, 4.00 equiv) in HFIP (63 μ L), (**\pm**)-**4k** was obtained after column chromatography (PE-EtOAc, 80:20 with 1% of NEt₃) as an orange oil (23.2 mg, quant). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.55. ν_{max} (film)/cm⁻¹ 3095, 2923, 2851, 1718, 1510, 1408, 1390, 1369, 1273, 1106, 1086, 1045, 1000, 965, 824, 809, 745. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.49 (d, *J* = 1.6 Hz, 1H, ArCH, H1'), 7.43 (d, *J* = 2.2 Hz, 1H, ArCH, H3'), 6.21 (t, *J* = 2.1 Hz, 1H, ArCH, H2'), 5.16 (d, *J* = 14.9 Hz, 1H, CHH), 5.11 (d, *J* = 14.9 Hz, 1H, CHH), 4.48 (dd, *J* = 1.3, 2.4 Hz, 1H, FcCH, H5), 4.39 (dd, *J* = 1.3, 2.6 Hz, 1H, FcCH, H3), 4.26 (t, *J* = 2.4 Hz, 1H, FcCH, H4), 4.17 (s, 5H, Cp). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ (ppm) 139.2 (ArCH, C1'), 128.9 (ArCH, C3'), 105.6 (ArCH, C2'), 84.4 (FcC, C2), 75.3 (FcCH, C5), 71.9 (Cp), 69.8 (FcCH, C4), 68.6 (FcCH, C3), 51.9 (CH₂), 44.7 (FcC, C1). Mass: 392 [M], 327 [Fc(I)CH₃ + H], 265 [M-I]. Anal. Calcd for C₁₄H₁₃FeIN₂: C, 42.89; H, 3.34; N, 7.15. Found: C, 42.92; H, 3.39; N, 7.18.

(S_p)-1-Iodo-2-(N-pyrazolinomethyl)ferrocene ((S_p)-4k**):** By following the general procedure A from compound (**S_p**)-**2** (38.4 mg, 0.10 mmol, 1.00 equiv) and pyrazole (27.3 mg, 0.40 mmol, 4.00 equiv) in HFIP (63 μ L), (**S_p**)-**4k** was obtained after column chromatography (PE-EtOAc, 80:20 with 1% of NEt₃) as an orange oil (36.0 mg, 92%, 94:6 er). Analytical data analogous to racemic compound. [α]_D +10.9 (c 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IC-3 column, hexane/iPrOH: 90:10, 0.8 mL·min⁻¹, 20 °C, λ = 254 nm, t (major) = 11.86 min, t (minor) = 13.36 min.

(\pm)-1-Iodo-2-(N-imidazolinomethyl)ferrocene ((\pm)-4l**):** By following the general procedure A from compound (**\pm**)-**2** (154 mg, 0.40 mmol, 1.00 equiv) and imidazole (109 mg, 1.60 mmol, 4.00 equiv) in HFIP (421 μ L), (**\pm**)-**4l** was obtained after column chromatography (PE-EtOAc, 60:40 to 20:80 with 2% of NEt₃) as an orange solid (104 mg, 66%). Mp 100-102 °C. R_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.41. ν_{max} (film)/cm⁻¹ 3095, 1504, 1437, 1366, 1276, 1242, 1227, 1104, 1066, 1026, 999, 969, 906, 831, 817, 809, 768, 741. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.56 (br s, 1H, ArCH, H1'), 7.04 (br s, 1H, ArCH, H2'), 6.99 (br s, 1H, ArCH, H3'), 4.97 (d, *J* = 14.5 Hz, 1H, CHH), 4.89 (d, *J* = 14.5 Hz, 1H, CHH), 4.49 (s, 1H, FcCH, H4 or H5), 4.25 (s, 3H, H3 and H4 or H5), 4.17 (s, 5H, Cp). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 137.2 (ArCH, C1'), 129.6 (ArCH, C2'), 119.2 (ArCH, C3'), 84.4 (FcC, C2), 75.5 (FcCH, C4 or C5), 71.9 (Cp), 69.7 (FcCH, C4 or C5), 68.1 (FcCH, C3), 47.1 (CH₂), 44.2 (FcC, C1). Anal. Calcd for C₁₄H₁₃FeIN₂: C, 42.89; H, 3.34; N, 7.15. Found: C, 42.80; H, 3.31; N, 7.05.

(\pm)-1-Iodo-2-(N-1,2,4-triazolinomethyl)ferrocene ((\pm)-4m**):** By following the general procedure A from compound (**\pm**)-**2** (115 mg, 0.30 mmol, 1.00 equiv) and 1,2,4-triazole (41.5 mg, 0.60 mmol, 2.00 equiv) in HFIP (316 μ L), (**\pm**)-**4m** was obtained after column chromatography (PE-EtOAc, 80:20 with 2% of NEt₃) as an orange solid (99 mg, 84%). Mp 115-117 °C. R_f (eluent: PE/EtOAc 70:30, 5 drops of NEt₃) = 0.29. ν_{max} (film)/cm⁻¹ 3113, 2990, 1503, 1429, 1371, 1347, 1279, 1239, 1201, 1133, 1105, 1019, 1000, 957, 869, 843, 825, 808, 778, 711. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (s, 1H, ArCH, H2'), 7.91 (s, 1H, ArCH, H1'), 5.20 (d, *J* = 14.7 Hz, 1H, CHH), 5.14 (d, *J* = 14.7 Hz, 1H, CHH), 4.51 (dd, *J* = 1.3, 2.3 Hz, 1H, FcCH, H5), 4.41 (dd, *J* = 1.3, 2.3 Hz, 1H, H3), 4.30 (t, *J* = 2.6 Hz, 1H, FcCH, H4),

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4.18 (s, 5H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 151.9 (ArCH, C1'), 142.8 (ArCH, C2'), 82.5 (FcC, C2), 75.6 (FcCH, C5), 72.0 (Cp), 70.1 (FcCH, C4), 68.7 (FcCH, C3), 49.9 (CH_2), 44.4 (FcC, C1). Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{FeIN}_2$: C, 39.73; H, 3.08; N, 10.69. Found: C, 40.17; H, 2.94; N, 10.37.

(±)-1-Iodo-2-(N-2-thionobenzothiazolomethyl)ferrocene ((±)-4n): By following the general procedure A from compound **(±)-2** (115 mg, 0.30 mmol, 1.00 equiv) and 2-mercaptobenzothiazole (52.3 mg, 0.60 mmol, 2.00 equiv) in HFIP (316 μL), **(±)-4n** was obtained after column chromatography (PE-EtOAc, 80:20 with 1% of NEt_3) as an orange solid (113 mg, 76%). Mp 159–160 °C. R_f (eluent: PE/EtOAc 90:10) = 0.48. ν_{max} (film)/ cm^{-1} 3089, 2930, 1461, 1431, 1386, 1369, 1316, 1292, 1237, 1202, 1141, 1129, 1053, 969, 822, 804, 757. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.44 (d, $J = 7.7$ Hz, 1H, ArCH, H5'), 7.33–7.26 (m, 2H, 2 x ArCH, H2' and H3'), 7.24 (m, 1H, ArCH, H4'), 6.34 (d, $J = 15.3$ Hz, 1H, CHH), 4.82 (d, $J = 15.3$ Hz, 1H, CHH), 4.44 (s, 1H, FcH, H5), 4.43 (s, 1H, FcCH, H3), 4.25 (s, 5H, Cp), 4.15 (t, $J = 2.6$ Hz, 1H, FcH, H4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ (ppm) 189.9 (C=S), 141.3 (ArC, C1'), 127.5 (ArC, C6'), 127.0 (ArCH, C3'), 124.9 (ArCH, C4'), 121.3 (ArCH, C5'), 113.7 (ArCH, C2'), 83.6 (FcC, C2), 74.2 (FcCH, C5), 72.6 (Cp), 69.5 (FcCH, C4), 68.3 (FcCH, C3), 46.2 (CH_2), 43.9 (FcC, C1). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{FeIN}_2\text{S}_2$: C, 44.01; H, 2.87; N, 2.85; S, 13.06. Found: C, 43.77; H, 2.91; N, 2.35; S, 12.58. **Crystal data for (±)-4n**. $\text{C}_{18}\text{H}_{14}\text{FeIN}_2\text{S}_2$, $M = 491.17$, $T = 150$ K; monoclinic $C2/c$ (I.T.#15), $a = 18.761(2)$, $b = 14.6448(15)$, $c = 12.5847(14)$ Å, $\beta = 95.803(4)$ °, $V = 3440.0(6)$ Å³. $Z = 8$, $d = 1.897$ g·cm⁻³, $\mu = 2.911$ mm⁻¹. A final refinement on F^2 with 3908 unique intensities and 209 parameters converged at $\omega R^2 = 0.0533$ ($R_F = 0.0245$) for 3581 observed reflections with $I > 2\sigma(I)$. CCDC 2090456. **(±)-1-Iodo-2-(S-2-thionobenzothiazolomethyl)ferrocene ((±)-4'n)** was also isolated as an orange oil (9 mg, 6%). R_f (eluent: PE/EtOAc 90:10) = 0.66. ν_{max} (film)/ cm^{-1} 2918, 1455, 1424, 1308, 1237, 1105, 1075, 990, 956, 821, 806, 752, 724. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.93 (d, $J = 8.2$ Hz, 1H, ArCH, H2'), 7.76 (d, $J = 8.0$ Hz, 1H, ArCH, H5'), 7.43 (dt, $J = 0.9$, 8.2 Hz, 1H, ArCH, H3'), 7.30 (dt, $J = 0.9$, 8.0 Hz, 1H, ArCH, H4'), 4.64 (d, $J = 13.1$ Hz, 1H, CHH), 4.47 (dd, $J = 1.2$, 2.1 Hz, 1H, FcCH, H5), 4.45 (dd, $J = 1.4$, 2.4 Hz, 1H, FcCH, H3), 4.34 (d, $J = 13.3$ Hz, 1H, CHH), 4.21 (s, 6H, Cp and FcCH, Cp and H4). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 166.5 (C=N), 153.4 (ArC, C1'), 135.6 (ArC, C6'), 126.2 (ArCH, C3'), 124.4 (ArCH, C4'), 121.6 (ArCH, C2'), 121.2 (ArCH, C5'), 84.7 (FcC, C2), 75.0 (FcCH, C5), 72.0 (Cp), 69.3 (FcCH, C4), 68.4 (FcCH, C3), 45.2 (FcC, C1), 34.5 (CH_2).

(±)-1-Iodo-2-(N-indazolomethyl)ferrocene ((±)-4o): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and indazole (94.5 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4o** was obtained after column chromatography (PE-EtOAc, 90:10 to 70:30 with 2% of NEt_3) as an orange oil (79 mg, 44%). R_f (eluent: PE/EtOAc 90:10, 5 drops of NEt_3) = 0.48. ν_{max} (film)/ cm^{-1} 3093, 1614, 1498, 1463, 1417, 1368, 1252, 1168, 1105, 1059, 1028, 1001, 904, 823, 762, 737. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.03 (s, 1H, ArCH, H1'), 7.73 (d, $J = 8.1$ Hz, 1H, ArCH, H3'), 7.60 (d, $J = 8.6$ Hz, 1H, ArCH, H6'), 7.38 (t, $J = 8.2$ Hz, 1H, ArCH, H5'), 7.14 (t, $J = 7.6$ Hz, 1H, ArCH, H4'), 5.44 (d, $J = 15.3$ Hz, 1H, CHH), 5.34 (d, $J = 15.3$ Hz, 1H, CHH), 4.45 (dd, $J = 1.4$, 2.1 Hz, 1H, FcCH, H3), 4.32 (dd, $J = 1.4$, 2.3 Hz, 1H, FcCH, H5), 4.19 (t, $J = 2.5$ Hz, 1H, FcCH, H4), 4.14 (s, 5H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ (ppm) 139.4 (ArC, C7'), 133.3 (ArCH, C1'), 126.3 (ArCH, C6'), 124.1 (ArC, C2'), 121.1 (ArCH, C3'), 120.6 (ArCH, C4'), 109.8 (ArCH, C5'), 85.5 (FcC, C2), 74.8 (FcCH, C5), 71.9 (Cp), 69.4 (FcCH, C4), 68.2 (FcCH, C3), 49.1 (CH_2), 44.1 (FcC, C1). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{FeIN}_2$: C, 48.90; H, 3.42; N, 6.34. Found: C, 48.95; H, 3.49; N, 6.37. **(±)-1-Iodo-2-(N'-indazolomethyl)ferrocene ((±)-4o')** was also isolated as an orange solid (94 mg, 53%). Mp 111–113 °C. R_f (eluent: PE/EtOAc 90:10, 5 drops of NEt_3) = 0.34. ν_{max} (film)/ cm^{-1} 3095, 1624, 1512, 1465, 1434, 1423, 1375, 1333, 1294, 1145, 1129, 1105, 1002, 821, 810, 785, 755. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.92 (s, 1H, ArCH, H1'), 7.71 (d, $J = 8.7$ Hz, 1H, ArCH, H6'), 7.61 (d, $J = 8.6$ Hz, 1H, ArCH, H3'), 7.27 (t, $J = 7.4$ Hz, 1H, ArCH, H5'), 7.05 (t, $J = 7.4$ Hz, 1H, ArCH, H4'), 5.44 (s, 2H, CH_2), 4.51 (dd, $J = 1.1$, 2.0 Hz, 1H, FcCH, H5), 4.49 (dd, $J = 1.5$, 2.6 Hz, 1H, FcCH, H3), 4.29 (t, $J = 2.6$ Hz, 1H, FcCH, H4), 4.20 (s, 5H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4

MHz, CDCl_3): δ (ppm) 148.7 (ArC, C7'), 125.9 (ArCH, C5'), 122.3 (ArCH, C1'), 121.9 (ArC, C2'), 121.7 (ArCH, C4'), 120.3 (ArCH, C3'), 117.6 (ArCH, C6'), 84.4 (FcC, C2), 75.5 (FcCH, C5), 72.0 (Cp), 70.1 (FcCH, C4), 68.9 (FcCH, C3), 53.5 (CH_2), 44.9 (FcC, C1). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{FeIN}_2$: C, 48.90; H, 3.42; N, 6.34. Found: C, 48.81; H, 3.35; N, 6.21.

(±)-1-Iodo-2-(tert-butoxycarbonylaminoethyl)ferrocene ((±)-4p): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and *tert*-butylcarbamate (93.7 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4p** was obtained after column chromatography (PE-EtOAc, 90:10) as an orange oil (79 mg, 45%). R_f (eluent: PE/EtOAc 95:5) = 0.77. ν_{max} (film)/ cm^{-1} 3090, 2931, 1461, 1369, 1316, 1292, 1202, 1141, 1129, 1052, 969, 822, 804, 757. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ (ppm) 7.14 (t, $J = 6.6$ Hz, 1H, NH), 4.42 (s, 1H, FcCH, H5), 4.29 (s, 1H, FcCH, H3), 4.21 (s, 1H, FcCH, H4), 4.14 (s, 5H, Cp), 4.03 (dd, $J = 6.6$, 15.0 Hz, 1H, CHH), 3.76 (dd, $J = 6.6$, 15.0 Hz, 1H, CHH), 1.14 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO}-d_6$): δ (ppm) 155.5 (C=O), 87.8 (FcC, C2), 77.7 (Cq), 73.6 (FcCH, C5), 71.2 (Cp), 68.2 (FcCH, C4), 67.2 (FcCH, C3), 43.0 (FcC, C1), 39.7 (CH_2), 28.3 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{FeINO}_2$: C, 43.57; H, 4.57; N, 3.18. Found: C, 43.70; H, 4.71; N, 3.29.

(±)-1-Iodo-2-(allyloxymethyl)ferrocene ((±)-4q): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and allyl alcohol (54.5 μL , 46.5 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4q** was obtained after column chromatography (PE-EtOAc, 95:5) as an orange oil (49 mg, 32%). R_f (eluent: PE/EtOAc 95:5) = 0.63. ν_{max} (film)/ cm^{-1} 3090, 2850, 1645, 1446, 1410, 1368, 1287, 1252, 1230, 1191, 1105, 1077, 1055, 1000, 921, 819, 745. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 5.94 (m, 1H, $\text{HC}=\text{CH}_2$), 5.32 (dq, $J = 1.5$, 17.2 Hz, 1H, $\text{HC}=\text{CHH}$), 5.20 (dq, $J = 1.3$, 10.4 Hz, 1H, $\text{HC}=\text{CHH}$), 4.45 (dd, $J = 1.4$, 2.1 Hz, 1H, FcCH, H5), 4.37–4.32 (m, 3H, CH_2 and FcH, $\text{CH}_2\text{-Fc}$ and H3), 4.23 (t, $J = 2.4$ Hz, 1H, FcCH, H4), 4.14 (s, 5H, Cp), 4.03 (m, 2H, $\text{CH}_2\text{-CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 135.1 ($\text{HC}=\text{CH}_2$), 117.1 ($\text{HC}=\text{CH}_2$), 85.0 (FcC, C2), 75.3 (FcCH, C5), 71.6 (Cp), 71.3 ($\text{CH}_2\text{-CH}$), 69.4 (FcCH, C4), 68.8 (FcCF, C3), 68.4 ($\text{CH}_2\text{-Fc}$), 45.0 (FcC, C1). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{FeIO}$: C, 44.02; H, 3.96. Found: C, 44.05; H, 4.00.

(±)-1-Iodo-2-(1,1,1,3,3,3-hexafluoro-2-propoxymethyl)ferrocene ((±)-4r): A solution of compound **(±)-2** (50.0 mg, 0.13 mmol, 1.00 equiv) in HFIP (410 μL , 665 mg, 3.90 mmol, 30.0 equiv) was heated at 60 °C for 1 h in a pre-heated oil bath. The reaction mixture was cooled to rt and was poured onto 2 mL of EtOAc and 1 mL of NEt_3 . Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2 , using PE/EtOAc (14:1 to 10:1) with 1% of NEt_3 to give the title product **(±)-4r** as an orange solid (41.0 mg, 64%). Alternatively, **(±)-4r** can also be prepared from **(±)-1**: A solution of compound **(±)-1** (55.0 mg, 0.13 mmol, 1.00 equiv) in HFIP (410 μL , 665 mg, 3.90 mmol, 30.0 equiv) was heated at 60 °C for 1 h in a pre-heated oil bath. The reaction mixture was cooled to rt and was poured onto 2 mL of EtOAc and 1 mL of NEt_3 . Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2 , using PE/EtOAc (12:1 to 10:1) with 1% of NEt_3 to give the title product as an orange solid (59.0 mg, 92%). R_f (eluent: PE/EtOAc 14:1, 5 drops of NEt_3) = 0.69. Mp 53–55 °C. ν_{max} (film)/ cm^{-1} 3097, 2932, 1455, 1371, 1284, 1262, 1216, 1185, 1099, 1000, 971, 895, 870, 825. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 4.74 (d, $J = 11.7$ Hz, 1H, CHH), 4.72 (d, $J = 11.7$ Hz, 1H, CHH), 4.53 (dd, $J = 1.4$, 2.2 Hz, 1H, FcCH, H5), 4.37 (dd, $J = 1.3$, 2.3 Hz, 1H, FcCH, H3), 4.32 (t, $J = 2.5$ Hz, 1H, FcCH, H4), 4.21 (sept, $J = 6.0$ Hz, 1H, CH), 4.17 (s, 5H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) 121.7 (dq, $J = 30.6$, 284 Hz, 2 x CF_3), 82.1 (s, FcC, C2), 76.0 (s, FcCH, C5), 74.2 (sept, $J = 32.7$ Hz, CH), 72.4 (s, CH_2), 71.8 (Cp), 70.3 (s, FcCH, C2), 69.2 (s, FcCH, C3), 44.6 (s, FcC, C1). $^{19}\text{F}\{^1\text{H}\}$ NMR (283 MHz, CDCl_3): δ (ppm) -73.6 (m, 2 x CF_3). Mass: 492 [M]. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{FeF}_6\text{IO}$: C, 34.18; H, 2.25. Found: C, 34.53; H, 2.41. **Crystal data for (±)-4r**. $\text{C}_{14}\text{H}_{11}\text{FeF}_6\text{IO}$, $M = 491.98$, $T = 150$ K; monoclinic $C2/c$ (I.T.#15), $a = 42.045(8)$, $b = 7.5013(14)$, $c = 10.080(2)$ Å, $\beta = 102.947(7)$ °, $V = 3098.3(11)$ Å³. $Z = 8$, $d = 2.109$ g·cm⁻³,

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$\mu = 3.029 \text{ nm}^{-1}$. A final refinement on F^2 with 3540 unique intensities and 184 parameters converged at $\omega R(F^2) = 0.0688$ ($R(F) = 0.0304$) for 3074 observed reflections with $I > 2\sigma(I)$. CCDC 1898629.

(S_p)-1-Iodo-2-(1,1,1,3,3,3-hexafluoro-2-propoxymethyl)ferrocene ((S_p)-4r): By following a similar protocol, starting from compound **(S_p)-2** (50.0 mg, 0.13 mmol, 1.00 equiv, er 96:4), the title product was obtained as an orange solid (27.0 mg, 42%, er 96:4). Analytical data analogous to racemic compound. $[\alpha]_D^{25} -18.5$ (c 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IA-3 column, hexane/iPrOH: 99:1, 0.5 mL/min, 5 °C, $\lambda = 254 \text{ nm}$, t (major) = 11.64 min, t (minor) = 10.84 min. Alternatively, **(S_p)-4r** can also be prepared from **(S_p)-1**: By following a similar protocol, starting from compound **(S_p)-1** (55.0 mg, 0.13 mmol, 1.00 equiv), the title product was obtained as an orange solid (56.0 mg, 87.5%, er 95:5). Analytical data analogous to racemic compound. The enantiomeric ratio was determined on Chiralpak IA-3 column, hexane/iPrOH: 99:1, 0.5 mL·min⁻¹, 5 °C, $\lambda = 254 \text{ nm}$, t (major) = 11.72 min, t (minor) = 10.97 min.

(±)-1-Iodo-2-(diphenylphosphinomethyl)ferrocene ((±)-4s): By following the general procedure A from compound **(±)-2** (57.6 mg, 0.15 mmol, 1.00 equiv) and diphenylphosphine (104 μL , 112 mg, 0.60 mmol, 4.00 equiv) in HFIP (160 μL), **(±)-4s** was obtained after column chromatography (PE-EtOAc, 50:1) as an orange oil (68 mg, 89%). R_f (eluent: PE/EtOAc 20:1) = 0.67. ν_{max} (film)/cm⁻¹ 3069, 2921, 2245, 1952, 1885, 1724, 1585, 1479, 1432, 1408, 1365, 1105, 1026, 999, 950, 908, 818, 737, 693. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.47-7.39 (m, 4H, ArCH, 4 x H^{2'}), 7.36-7.31 (m, 6H, ArCH, 4 x H^{3'} and 2 x H^{4'}), 4.37 (dd, $J = 2.2, 1.4 \text{ Hz}$, 1H, FcCH, H⁵), 4.09 (s, 5H, Cp), 4.05 (t, $J = 2.5 \text{ Hz}$, 1H, FcCH, H⁴), 3.82 (s, 1H, FcCH, H³), 3.22 (d, $J = 14.4 \text{ Hz}$, 1H, C/H), 3.19 (d, $J = 14.4 \text{ Hz}$, 1H, C/H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 138.8 (d, $J = 15.3 \text{ Hz}$, ArC, C^{1'}), 138.2 (d, $J = 15.3 \text{ Hz}$, ArC, C^{1'}), 133.7 (d, $J = 19.8 \text{ Hz}$, ArCH, 2 x C^{2'}), 132.5 (d, $J = 17.9 \text{ Hz}$, ArCH, 2 x C^{2'}), 129.1 (s, ArCH, 2 x C^{4'}), 128.5 (d, $J = 4.5 \text{ Hz}$, ArCH, 4 x C^{3'}), 86.1 (d, $J = 15.4 \text{ Hz}$, FcC, C²), 74.1 (s, FcCH, C⁵), 71.9 (s, Cp), 68.3 (s, FcCH, C⁴), 67.9 (d, $J = 5.7 \text{ Hz}$, FcCH, C³), 48.7 (d, $J = 3.3 \text{ Hz}$, FcC, C¹), 30.6 (d, $J = 15.6 \text{ Hz}$, CH₂). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ (ppm) -13.8.

(S_p)-1-Iodo-2-(diphenylphosphinomethyl)ferrocene ((S_p)-4s): By following the general procedure A from compound **(S_p)-2** (38.4 mg, 0.1 mmol, 1.00 equiv) and diphenylphosphine (69.6 μL , 74.5 mg, 0.40 mmol, 4.00 equiv) in HFIP (106 μL), **(S_p)-4s** was obtained after column chromatography (PE-EtOAc, 50:1) as an orange oil (50.0 mg, 98%, 95:5 er). Analytical data analogous to racemic compound. $[\alpha]_D^{25} +3.54$ (c 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IA-3 column, hexane/iPrOH: 99:1, 0.8 mL·min⁻¹, 20 °C, $\lambda = 254 \text{ nm}$, t (major) = 6.21 min, t (minor) = 6.80 min.

(±)-1-Iodo-2-(3-(N-indolyl)methyl)ferrocene ((±)-4t): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and indole (94.0 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4t** was obtained after column chromatography (PE-EtOAc, 95:5 with 2% of NEt₃) as an orange solid (143 mg, 81%). R_f (eluent: PE/EtOAc 95:5) = 0.32. Mp 170-171 °C. ν_{max} (film)/cm⁻¹ 3411, 3089, 3053, 2892, 1615, 1455, 1418, 1403, 1354, 1335, 1221, 1102, 1088, 1011, 996, 958, 829, 804, 752. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.89 (br s, 1H, NH), 7.67 (d, $J = 7.7 \text{ Hz}$, 1H, ArCH, H^{4'}), 7.34 (d, $J = 8.1 \text{ Hz}$, 1H, ArCH, H^{7'}), 7.20 (dt, $J = 1.1, 8.1 \text{ Hz}$, 1H, ArCH, H^{6'}), 7.13 (dt, $J = 0.9, 7.7 \text{ Hz}$, 1H, ArCH, H^{5'}), 6.92 (m, 1H, ArCH, H^{1'}), 4.42 (dd, $J = 1.4, 2.3 \text{ Hz}$, 1H, FcCH, H⁵), 4.22 (dd, $J = 1.4, 2.3 \text{ Hz}$, 1H, FcCH, H³), 4.15 (s, 5H, Cp), 4.13 (t, $J = 2.3 \text{ Hz}$, 1H, FcCH, H⁴), 3.89 (s, 2H, CH₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 136.3 (ArC, C^{8'}), 127.4 (ArC, C^{3'}), 122.3 (ArCH, C^{1'}), 122.1 (ArCH, C^{6'}), 119.5 (ArCH, C^{5'}), 115.8 (ArC, C^{2'}), 111.2 (ArCH, C^{7'}), 89.5 (FcC, C²), 74.2 (FcCH, C⁵), 71.8 (Cp), 68.3 (FcCH, C⁴), 67.9 (FcCH, C³), 45.7 (FcC, C¹), 26.3 (CH₂). Anal. Calcd for C₁₉H₁₆FeIN: C, 51.74; H, 3.66; N, 3.18. Found: C, 51.54; H, 3.53; N, 2.98.

(±)-1-Iodo-2-(N-methyl-3-indolylmethyl)ferrocene ((±)-4u): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and N-methylindole (105 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4u** was obtained after column chromatography (PE-EtOAc, 95:5 with 2% of NEt₃) and trituration in pentane as an orange solid (146 mg, 80%). It can also be prepared on a larger scale by following the general procedure A from compound **(±)-2** (499 mg, 1.30 mmol, 1.00 equiv) and N-methylindole (341 mg, 2.60 mmol, 2.00 equiv) in HFIP (1.40 mL). Compound **(±)-4u** was obtained as an orange solid (499 mg, 84%). R_f (eluent: PE/EtOAc 95:5) = 0.53. Mp 136-137 °C. ν_{max} (film)/cm⁻¹ 3093, 2929, 1614, 1472, 1432, 1368, 1328, 1231, 1204, 1156, 1102, 1030, 997, 961, 807, 742. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.66 (d, $J = 8.0 \text{ Hz}$, 1H, ArCH, H^{4'}), 7.28 (d, $J = 8.1 \text{ Hz}$, 1H, ArCH, H^{7'}), 7.22 (dt, $J = 0.8, 7.2 \text{ Hz}$, 1H, ArCH, H^{6'}), 7.12 (dt, $J = 1.0, 7.0 \text{ Hz}$, 1H, ArCH, H^{5'}), 6.76 (s, 1H, ArCH, H^{1'}), 4.42 (dd, $J = 1.3, 2.3 \text{ Hz}$, 1H, FcCH, H⁵), 4.23 (dd, $J = 1.3, 2.3 \text{ Hz}$, 1H, FcCH, H³), 4.16 (s, 5H, Cp), 4.14 (t, $J = 2.3 \text{ Hz}$, 1H, FcCH, C⁴), 3.90 (d, $J = 16.7 \text{ Hz}$, 1H, C/H), 3.86 (d, $J = 16.7 \text{ Hz}$, 1H, C/H), 3.72 (s, 3H, CH₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 137.0 (ArC, C^{8'}), 127.7 (ArC, C^{3'}), 127.0 (ArCH, C^{1'}), 121.6 (ArCH, C^{6'}), 119.2 (ArCH, C^{4'}), 118.8 (ArCH, C^{5'}), 114.3 (ArC, C^{2'}), 109.3 (ArCH, C^{7'}), 89.7 (FcC, C²), 74.2 (FcCH, C⁵), 71.8 (Cp), 68.3 (FcCH, C⁴), 67.9 (FcCH, C³), 45.7 (FcC, C¹), 32.8 (CH₃), 26.3 (CH₂). Anal. Calcd for C₂₀H₁₈FeIN: C, 52.78; H, 3.99; N, 3.08. Found: C, 52.90; H, 4.01; N, 3.15. **Crystal data for (±)-4u.** C₂₀H₁₈FeIN, $M = 455.10$, $T = 150 \text{ K}$; monoclinic $P2_1/c$ (I.T.#14), $a = 12.3344(7)$, $b = 11.2470(6)$, $c = 12.5667(7) \text{ \AA}$, $\beta = 95.672(2)^\circ$, $V = 1734.78(17) \text{ \AA}^3$, $Z = 4$, $d = 1.743 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 2.647 \text{ mm}^{-1}$. A final refinement on F^2 with 3895 unique intensities and 209 parameters converged at $\omega R(F^2) = 0.0774$ ($R(F) = 0.0355$) for 3384 observed reflections with $I > 2\sigma(I)$. CCDC 2090457.

(±)-1-Iodo-2-(3-benzothiophenylmethyl)ferrocene ((±)-4v): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and benzothiophene (107 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4v** was obtained after column chromatography (PE-EtOAc, 15:1) as an orange solid (45 mg, 24%). R_f (eluent: PE/EtOAc 90:10) = 0.80. Mp 133-135 °C. ν_{max} (film)/cm⁻¹ 3088, 1456, 1426, 1406, 1281, 1252, 1133, 1104, 1018, 998, 958, 861, 825, 807, 758, 742, 727. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.85 (d, $J = 7.5 \text{ Hz}$, 1H, ArCH, H^{7'}), 7.84 (d, $J = 7.5 \text{ Hz}$, 1H, ArCH, H^{4'}), 7.41 (t, $J = 7.5 \text{ Hz}$, 1H, H^{6'}), 7.35 (t, $J = 7.5 \text{ Hz}$, 1H, ArCH, H^{5'}), 6.96 (s, 1H, ArCH, H^{1'}), 4.46 (s, 1H, FcCH, H⁵), 4.19 (s, 1H, FcCH, H³), 4.18 (s, 1H, H⁵), 4.16 (s, 5H, Cp), 3.96 (s, 2H, CH₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 140.6 (ArC, C^{8'}), 138.8 (ArC, C^{3'}), 135.5 (ArC, C^{2'}), 124.3 (ArCH, C^{5'}), 124.0 (ArCH, C^{6'}), 123.0 (ArCH, C^{7'}), 122.9 (ArCH, C^{1'}), 121.9 (ArCH, C^{4'}), 87.9 (FcC, C²), 74.6 (FcCH, C⁵), 71.9 (Cp), 68.6 and 68.1 (FcCH, C³ and C⁴), 45.7 (FcC, C¹), 29.7 (CH₂). Anal. Calcd for C₁₉H₁₅FeIS: C, 49.81; H, 3.30; S, 7.00. Found: C, 49.96; H, 3.28; S, 6.82. **Crystal data for (±)-4v.** C₁₉H₁₅FeIS, $M = 458.12$, $T = 150 \text{ K}$; monoclinic $P2_1/c$ (I.T.#14), $a = 10.3379(9)$, $b = 11.6871(9)$, $c = 13.8680(12) \text{ \AA}$, $\beta = 101.121(3)^\circ$, $V = 1644.1(2) \text{ \AA}^3$, $Z = 4$, $d = 1.851 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 2.915 \text{ mm}^{-1}$. A final refinement on F^2 with 3730 unique intensities and 169 parameters converged at $\omega R(F^2) = 0.1460$ ($R(F) = 0.0628$) for 3196 observed reflections with $I > 2\sigma(I)$. CCDC 2090458.

(±)-1-Iodo-2-(2-benzofuranylmethyl)ferrocene ((±)-4w): By following the general procedure A from compound **(±)-2** (154 mg, 0.40 mmol, 1.00 equiv) and benzofurane (94.5 mg, 0.80 mmol, 2.00 equiv) in HFIP (421 μL), **(±)-4w** was obtained after column chromatography (PE-EtOAc, 20:1) as an orange oil (65 mg, 36%). R_f (eluent: PE/EtOAc 90:10) = 0.82. ν_{max} (film)/cm⁻¹ 3087, 1599, 1586, 1453, 1418, 1252, 1167, 1105, 1000, 950, 907, 823, 801, 729. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.49 (d, $J = 7.3 \text{ Hz}$, 1H, ArCH, H^{4'}), 7.45 (d, $J = 8.0 \text{ Hz}$, 1H, ArCH, H^{7'}), 7.23 (dt, $J = 1.2, 8.0 \text{ Hz}$, 1H, ArCH, H^{6'}), 7.19 (t, $J = 0.8, 7.3 \text{ Hz}$, 1H, ArCH, H^{5'}), 6.39 (s, 1H, ArCH, H^{2'}), 4.45 (dd, $J = 1.2, 1.9 \text{ Hz}$, 1H, FcCH, H⁵), 4.28 (dd, $J = 1.2, 1.9 \text{ Hz}$, 1H, FcCH, H³), 4.19 (t, $J = 2.4 \text{ Hz}$, 1H, FcCH, H⁴), 4.15 (s, 5H, Cp), 3.89 (s, 2H, CH₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 157.1 (ArC, C^{1'}), 154.8 (ArC, C^{8'}), 128.9 (ArC, C^{3'}), 123.5 (ArCH, C^{6'}), 122.7 (ArCH, C^{5'}), 120.6 (ArCH, C^{4'}), 111.0 (ArCH, C^{7'}), 103.2 (ArCH, C^{2'}), 85.9 (FcC, C²), 74.5 (FcCH, C⁵), 71.9 (Cp), 68.6 (FcCH, C⁴), 67.9 (FcCH, C³),

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45.2 (FcC, C1), 29.9 (CH₂). Anal. Calcd for C₁₉H₁₅FeIO: C, 51.62; H, 3.42. Found: C, 51.89; H, 3.37.

(±)-1-Iodo-3-(*N*-morpholinomethyl)ferrocene ((±)-7a): By following the general procedure A from compound **(±)-5** (115 mg, 0.30 mmol) and morpholine (52.5 μL, 52.3 mg, 0.60 mmol) in HFIP (316 μL), **(±)-7a** was obtained after column chromatography (PE-EtOAc, 80:20 to 20:80 with 1% of NEt₃) as an orange solid (111 mg, 90%). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.22. Mp 99–100 °C. ν_{\max} (film)/cm⁻¹ 2928, 2861, 1799, 2751, 1449, 1349, 1330, 1284, 123, 1155, 1104, 1070, 1029, 997, 907, 871, 861, 851, 819, 800. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.44 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.38 (dd, *J* = 1.2, 1.9 Hz, 1H, FcCH, H5); 4.17 (dd, *J* = 1.2, 1.9 Hz, 1H, FcCH, H4), 4.14 (s, 5H, Cp), 3.65 (t, *J* = 4.7 Hz, 4H, 2 x CH₂O), 3.30 (d, *J* = 12.9 Hz, 1H, CHH), 3.24 (d, *J* = 12.9 Hz, 1H, CHH), 2.38 (t, *J* = 4.7 Hz, 4H, 2 x CH₂N). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 83.6 (FcC, C3), 76.6 (FcCH, C2), 74.7 (FcCH, C5), 71.8 (Cp), 71.0 (FcCH, C4), 67.0 (2 x CH₂O), 58.5 (CH₂), 53.3 (2 x CH₂N), 39.7 (FcC, C1). Anal. Calcd for C₁₅H₁₈FeINO: C, 43.83; H, 4.41; N, 3.41. Found: C, 43.82; H, 4.34; N, 3.31. **Crystal data for (±)-7a.** C₁₅H₁₈FeINO, *M* = 411.05, *T* = 150 K; monoclinic *P*2₁/*n* (I.T.#14), *a* = 6.8814(4), *b* = 26.8918(16), *c* = 7.9563(5) Å, β = 94.774(2)°, *V* = 1467.23(15) Å³. *Z* = 4, *d* = 1.861 g·cm⁻³, μ = 3.123 mm⁻¹. A final refinement on *F*² with 3326 unique intensities and 172 parameters converged at $\omega R(F^2)$ = 0.0603 (*R*(*F*) = 0.0309) for 3018 observed reflections with *I* > 2 σ (*I*). CCDC 2090459.

(±)-1-Iodo-3-(*N*-pyrazolinomethyl)ferrocene ((±)-7b): By following the general procedure A from compound **(±)-5** (38.4 mg, 0.10 mmol) and pyrazole (13.7 mg, 0.20 mmol) in HFIP (106 μL), **(±)-7b** was obtained after column chromatography (PE-EtOAc, 75:25 with 1% of NEt₃) as an orange solid (39.1 mg, quant). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.38. Mp 92–94 °C. ν_{\max} (film)/cm⁻¹ 2923, 1511, 1444, 1395, 1353, 1272, 1237, 1216, 1105, 1085, 1049, 998, 968, 871, 826, 764, 706. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.48 (d, *J* = 1.1 Hz, 1H, ArCH, H1'), 7.32 (d, *J* = 2.0 Hz, 1H, ArCH, H3'), 6.21 (t, *J* = 2.0 Hz, 1H, ArCH, H2'), 4.98 (d, *J* = 14.7 Hz, 1H, CHH), 4.94 (d, *J* = 14.7 Hz, 1H, CHH), 4.49 (s, 1H, FcCH, H2), 4.40 (dd, *J* = 1.1, 2.0 Hz, 1H, FcCH, H5), 4.24 (t, *J* = 1.7 Hz, 1H, FcCH, H4), 4.15 (s, 5H, Cp). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 139.3 (ArCH, H1'), 128.6 (ArCH, C3'), 105.8 (ArCH, C2'), 84.4 (FcC, C3), 75.2 and 75.1 (FcCH, C2 and C5), 72.1 (Cp), 69.6 (FcCH, C4), 51.2 (CH₂), 39.6 (FcC, C1). Mass: 392 [M], 265 [M-]. Anal. Calcd for C₁₄H₁₃FeIN₂: C, 42.89; H, 3.34; N, 7.15. Found: C, 42.95; H, 3.48; N, 7.18. **Crystal data for (±)-7b.** C₁₄H₁₃FeIN₂, *M* = 392.01, *T* = 150 K; monoclinic *P*2₁/*c* (I.T.#14), *a* = 17.842(3), *b* = 7.5959(11), *c* = 9.9836(19) Å, β = 92.201(8)°, *V* = 1352.0(4) Å³. *Z* = 4, *d* = 1.926 g·cm⁻³, μ = 3.381 mm⁻¹. A final refinement on *F*² with 3091 unique intensities and 139 parameters converged at $\omega R(F^2)$ = 0.0984 (*R*(*F*) = 0.0395) for 2694 observed reflections with *I* > 2 σ (*I*). CCDC 1898630.

***N,N*-Dimethyl-*N,N'*-(3-iodoferrocenylmethyl)ethylenediamine ((±)-7c):** By following the general procedure A from compound **(±)-5** (84.5 mg, 0.22 mmol, 1.00 equiv) and *N,N*-dimethylethylenediamine (11.0 μL, 8.81 mg, 0.10 mmol, 0.45 equiv) in HFIP (210 μL), **(±)-7c** was obtained after column chromatography (PE-EtOAc, 50:50 to 0:100 with 2% of NEt₃) as an orange oil (52 mg, 70%). R_f (eluent: PE/EtOAc 20:80, 5 drops of NEt₃) = 0.18. ν_{\max} (film)/cm⁻¹ 2775, 1454, 1410, 1358, 1344, 1318, 1270, 1237, 1157, 1118, 1103, 1029, 1013, 868, 834, 821. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.39 (m, 2H, FcCH, 2 x H2), 4.35 (m, 2H, FcCH, 2 x H5), 4.11 (s, 12H, Cp and FcCH, 2 x Cp and 2 x H4), 3.31 (d, *J* = 13.3 Hz, 2H, 2 x CHH), 3.24 (d, *J* = 13.3 Hz, 2H, 2 x CHH), 2.33 (s, 4H, 2 x CH₂N), 2.12 (s, 6H, 2 x CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 84.0 (FcCH, 2 x C3), 76.7 (FcCH, 2 x C2), 74.6 (FcCH, 2 x C5), 71.8 (2 x Cp), 71.0 (2 x FcCH, C4), 57.2 (CH₂-Fc), 57.1 (CH₂-Fc), 54.0 (CH₂N), 53.9 (CH₂N), 42.4 (CH₃), 42.3 (CH₃), 39.8 (FcC, 2 x C1). Anal. Calcd for C₂₆H₃₀FeI₂N₂: C, 42.43; H, 4.11; N, 3.81. Found: C, 42.50; H, 4.21; N, 3.87.

(±)-1-Iodo-3-(((1,1,1,3,3,3-hexafluoro-2-propoxymethyl)ferrocene ((±)-7d): A solution of compound **(±)-5** (38.4 mg, 0.10 mmol, 1.00 equiv) in HFIP (315 μL, 504 mg, 3.00 mmol, 30.0 equiv) was heated at 60 °C for 1

h in a pre-heated oil bath. The reaction mixture was cooled to rt and was poured onto 2 mL of EtOAc and 1 mL of NEt₃. Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE/EtOAc (20:1) with 2% of NEt₃ to give the title product as an orange solid (26.1 mg, 53%). R_f (eluent: PE/EtOAc 10:1) = 0.69. Mp 124–126 °C. ν_{\max} (film)/cm⁻¹ 2924, 1462, 1399, 1367, 1288, 1206, 1195, 1117, 1093, 1031, 1000, 963, 895, 873, 827, 758, 737, 683. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.62 (d, *J* = 11.2 Hz, 1H, CHH), 4.58 (d, *J* = 11.2 Hz, 1H, CHH), 4.55 (m, 1H, FcCH, H2), 4.51 (m, 1H, FcCH, H5), 4.29 (s, FcCH, H4), 4.22 (s, 5H, Cp), 4.14 (sept, 6.0 Hz, 1H, CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 121.7 (d, *J* = 284.0 Hz, 2 x CF₃), 81.6 (s, FcC, C3), 75.8 and 75.7 (s, 2 x FcH, C2 and C5), 74.4 (sept, *J* = 32.5 Hz, CH), 72.0 (s, CH₂), 71.9 (s, Cp), 70.2 (s, FcCH, C4), 39.6 (s, FcC, C1). ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ (ppm) -73.7 (m, 2 x CF₃). Mass: 492 [M]. Anal. Calcd for C₁₄H₁₁F₆FeIO: C, 34.18; H, 2.25. Found: C, 34.22; H, 2.31.

(±)-1-Iodo-3-(diphenylphosphinomethyl)ferrocene ((±)-7e): By following the general procedure A from compound **(±)-2** (57.6 mg, 0.15 mmol, 1.00 equiv) and diphenylphosphine (104 μL, 112 mg, 0.60 mmol, 4.00 equiv) in HFIP (160 μL), **(±)-7e** was obtained after column chromatography (PE-EtOAc, 50:1) as an orange oil (60 mg, 78%). R_f (eluent: PE/EtOAc 20:1) = 0.79. ν_{\max} (film)/cm⁻¹ 3070, 3051, 2923, 1584, 1480, 1460, 1432, 1409, 1376, 1105, 1067, 1025, 999, 933, 870, 738, 721. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.38–7.34 (m, 4H, ArCH), 7.32–7.30 (m, 6H, ArCH), 4.22 (dd, *J* = 1.2, 2.2 Hz, 1H, FcCH, H5), 4.16 (s, 1H, FcCH, H2), 4.10 (s, 5H, Cp), 3.87 (t, *J* = 1.7 Hz, 1H, FcCH, H4), 3.07 (d, *J* = 14.2 Hz, 1H, CHH), 3.03 (d, *J* = 14.2 Hz, 1H, CHH). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 138.6 (d, *J* = 11.4 Hz, ArC, C1'), 138.5 (d, *J* = 11.3 Hz, ArC, C1'), 133.1 (d, *J* = 19.5 Hz, ArCH, 2 x C2'), 132.9 (d, *J* = 19.0 Hz, ArCH, 2 x C2'), 129.0 (d, *J* = 5.2 Hz, ArCH, 2 x C4'), 128.6 (d, *J* = 6.6 Hz, ArCH, 4 x C3'), 85.6 (d, *J* = 15.6 Hz, FcC, C3), 75.7 (d, *J* = 4.2 Hz, FcCH, C2), 73.9 (s, FcCH, C5), 72.1 (s, Cp), 69.9 (d, *J* = 4.4 Hz, FcCH, C4), 39.8 (s, FcC, C1), 30.1 (d, *J* = 15.3 Hz, CH₂). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ (ppm) -12.6.

1-Iodo-1'-(*N*-morpholinomethyl)ferrocene (8a): By following the general procedure A from compound **6** (768 mg, 2.00 mmol) and morpholine (350 μL, 349 mg, 4.00 mmol) in HFIP (2.10 mL), **8a** was obtained after column chromatography (PE-EtOAc, 50:50 to 30:70 with 1% of NEt₃) as an orange solid (787 mg, 96%). R_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.38. Mp 73–74 °C. ν_{\max} (film)/cm⁻¹ 2922, 2864, 2793, 1446, 1392, 1344, 1326, 1283, 1265, 1126, 1107, 1071, 1002, 859, 819, 801. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.33 (t, *J* = 1.7 Hz, 2H, FcCH, H2 and H5), 4.16 (t, *J* = 1.8 Hz, 2H, FcCH, H3' and H4'), 4.13 (t, *J* = 1.8 Hz, 2H, FcCH, H2' and H5'), 4.11 (t, *J* = 1.7 Hz, 2H, FcCH, H3 and H4), 3.66 (t, *J* = 4.6 Hz, 4H, 2 x CH₂O), 3.38 (s, 2H, CH₂), 2.41 (t, *J* = 4.6 Hz, 4H, 2 x CH₂N). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 83.9 (FcC, C1'), 75.3 (FcCH, C2 and C5), 73.5 (FcCH, C2' and C5'), 71.4 (FcCH, C3' and C4'), 69.5 (FcCH, C3 and C4), 67.0 (2 x CH₂O), 58.1 (CH₂), 53.3 (2 x CH₂N), 40.4 (FcC, C1). Anal. Calcd for C₁₅H₁₈FeINO: C, 43.83; H, 4.41; N, 3.41. Found: C, 43.67; H, 4.06; N, 3.52. **Crystal data for 8a.** C₁₅H₁₈FeINO, *M* = 411.05, *T* = 150 K; monoclinic *P*2₁/*n* (I.T.#14), *a* = 6.2155(5), *b* = 9.6683(6), *c* = 24.5900(18) Å, β = 94.916(2)°, *V* = 1472.26(18) Å³. *Z* = 4, *d* = 1.854 g·cm⁻³, μ = 3.112 mm⁻¹. A final refinement on *F*² with 3357 unique intensities and 172 parameters converged at $\omega R(F^2)$ = 0.0550 (*R*(*F*) = 0.0228) for 3183 observed reflections with *I* > 2 σ (*I*). CCDC 2090460.

(*R,S*)-1-Iodo-2-(*N*-morpholinoethyl)ferrocene ((*R,S*)-10): By following the general procedure A from compound **(*R,S*)-9b** (119 mg, 0.30 mmol) and morpholine (52.5 μL, 52.3 mg, 2.00 mmol) in HFIP (316 μL), **(*R,S*)-10** was obtained after column chromatography (PE-EtOAc, 90:10 to 70:30 with 2% of NEt₃) as an orange solid (100 mg, 78%). R_f (eluent: PE/EtOAc 80:20, 5 drops of NEt₃) = 0.62. Mp 115–116 °C. [α]_D²⁰ -32.4 (c 0.01 in CHCl₃). ν_{\max} (film)/cm⁻¹ 2945, 2884, 2844, 2826, 1438, 1378, 1283, 1253, 1229, 1128, 1116, 1029, 1002, 958, +20, 854, 819, 762, 725. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.47 (s, 1H, FcCH, H5), 4.23 (s, 1H, FcCH, H4), 4.13 (s, 1H, FcCH, H3), 4.12 (s, 5H, Cp), 3.67 (q, *J* = 6.8 Hz, 1H, CH), 3.60 (t, *J* =

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4.3 Hz, 4H, 2 x CH₂O), 2.49-2.45 and 2.39-2.36 (m, 2H, 2 x CH₂N), 1.51 (d, *J* = 6.8 Hz, 3H, CH₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 89.7 (FcC, C2), 74.7 (FcCH, C5), 71.8 (Cp), 68.3 (FcCH, C4), 67.5 (2 x CH₂O), 66.0 (FcCH, C3), 58.2 (CH), 49.3 (2 x CH₂N), 45.6 (FcC, C1), 15.6 (CH₃). Anal. Calcd for C₁₆H₂₀FeINO: C, 45.21; H, 4.74; N, 3.29. Found: C, 45.29; H, 4.79; N, 3.33. **Crystal data for (R_fS_p)-10.** C₁₆H₂₀FeINO, *M* = 425.08, *T* = 150 K; orthorhombic *P*2₁2₁2₁ (I.T.#19), *a* = 7.3714(5), *b* = 11.6599(6), *c* = 18.1493(12) Å, *V* = 1559.93(17) Å³. *Z* = 4, *d* = 1.810 g·cm⁻³, *μ* = 2.941 mm⁻¹. A final refinement on *F*² with 3564 unique intensities and 182 parameters converged at ω*R*² = 0.0446 (*R*_F = 0.0202) for 3456 observed reflections with *I* > 2σ(*I*). CCDC 2090461.

General procedure B: Li/I exchange-trapping sequence. tBuLi (1.6M, 2.00 equiv) was added dropwise to a solution of the required substrate (1.00 equiv) in THF (10 mL per mmol) at -80 °C. The reaction mixture was stirred at the same temperature for 10 min before the required electrophile was added. After addition, the reaction mixture was stirred at the same temperature for 10 min before being warmed to rt. Methanol was added and volatiles were removed under vacuum to give the crude product. This was purified by column chromatography over SiO₂ (eluant given in the product description) to give the title product.

(±)-1-Diphenylphosphino-2-(*N*-morpholinomethyl)ferrocene ((±)-11a): By following the general procedure B from compound (±)-4a (205 mg, 0.50 mmol, 1.00 equiv) and diphenylchlorophosphine (111 μL, 132 mg, 0.6 mmol), (±)-11a was obtained after column chromatography (PE/EtOAc, 70:30 to 50:50 with 1% of NEt₃) as an orange solid (101 mg, 43%). *R*_f (eluent: PE/EtOAc 50:50, 5 drops of NEt₃) = 0.66. Mp 140-142 °C. *v*_{max} (film)/cm⁻¹ 2956, 2928, 2861, 2796, 1475, 1431, 1348, 1327, 1289, 1132, 1110, 1004, 861, 809, 751, 698. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.58-7.55 (m, 2H, ArCH, 2 x H^{2'}), 7.38-7.36 (m, 3H, ArCH, 2 x H^{3'} and H^{4'}), 7.25-7.20 (m, 5H, ArCH, 2 x H^{2'} and 2 x H^{3'} and H^{4'}), 4.39 (s, 1H, FcCH, H3), 4.25 (t, *J* = 2.1 Hz, 1H, FcCH, H4), 3.99 (s, 5H, Cp), 3.87 (dd, *J* = 12.6, 2.0 Hz, 1H, CHH), 3.81 (s, 1H, FcCH, H5), 3.25-3.22 (m, 2H, CH₂O), 3.11-3.09 (m, 3H, CHH + CH₂O), 2.23-2.15 (m, 4H, 2 x CH₂N). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 140.3 (d, *J* = 8.4 Hz, ArC, C^{1'}), 137.9 (d, *J* = 8.5 Hz, 1H, ArC, C^{1'}), 135.1 (d, *J* = 21.1 Hz, ArCH, 2 x C^{2'}), 132.8 (d, *J* = 19.0 Hz, ArCH, 2 x C^{2'}), 129.1 (s, ArCH, C^{4'}), 128.1 (d, *J* = 7.6 Hz, ArCH, 2 x C^{3'}), 127.9 (d, *J* = 5.6 Hz, ArCH, 2 x C^{3'}), 127.8 (s, ArCH, C^{4'}), 89.5 (d, *J* = 24.9 Hz, FcC, C2), 77.3 (multiplicity hidden, FcC, C1), 73.3 (d, *J* = 3.6 Hz, FcCH, C3), 72.1 (d, *J* = 4.3 Hz, FcCH, C5), 69.8 (s, Cp), 69.1 (s, FcCH, C4), 66.8 (s, 2 x CH₂O), 57.7 (d, *J* = 7.6 Hz, CH₂), 53.1 (s, 2 x CH₂N). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ (ppm) -23.9.

(±)-1-Dicyclohexylphosphino-2-(*N*-morpholinomethyl)ferrocene ((±)-11b): By following the general procedure B from compound (±)-4a (411 mg, 1.00 mmol, 1.00 equiv) and dicyclohexylchlorophosphine (265 μL, 279 mg, 1.20 mmol), (±)-11b was obtained after column chromatography (PE/EtOAc, 95:5 to 90:10 with 1% of NEt₃) as an orange solid (360 mg, 75%). *R*_f (eluent: PE/EtOAc 95:5, 5 drops of NEt₃) = 0.25. Mp 145-147 °C. *v*_{max} (film)/cm⁻¹ 2919, 2848, 2794, 1442, 1348, 1327, 1286, 1264, 1115, 1069, 1030, 1005, 988, 852, 825, 803. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.26 (s, 1H, FcCH, H3), 4.23 (t, *J* = 2.2 Hz, 1H, FcCH, H4), 4.08 (s, 1H, FcCH, H5), 4.06 (s, 5H, Cp), 3.80 (dd, *J* = 2.3, 12.5 Hz, 1H, CHH), 3.66-3.58 (m, 4H, 2 x CH₂O), 3.01 (d, *J* = 12.5 Hz, 1H, CHH), 2.49-2.47 (m, 2H, CH₂N), 2.38-2.33 (m, 3H, CH₂N and CH), 2.07-2.03 (m, 1H, CH), 2.03-1.97 (m, 1H), 1.90-1.85 (m, 3H), 1.74 (d, *J* = 11.3 Hz, 1H), 1.68-1.65 (m, 3H), 1.62-1.58 (m, 2H), 1.45-1.35 (m, 4H), 1.32-1.25 (m, 2H), 1.22-1.04 (m, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 87.5 (d, *J* = 20.6 Hz, FcC, C1), 79.7 (d, *J* = 16.7 Hz, FcC, C2), 72.6 (d, *J* = 2.4 Hz, FcCH, C3), 70.6 (d, *J* = 2.0 Hz, FcCH, C5), 69.9 (s, Cp), 68.2 (FcCH, C4), 67.1 (s, 2 x CH₂O), 57.9 (d, *J* = 9.0 Hz, CH₂), 53.5 (s, 2 x CH₂N), 36.5 (d, *J* = 12.6 Hz, CH), 34.0 (d, *J* = 10.2 Hz, 1H, CH), 32.9 (d, *J* = 19.0 Hz, CH₂), 31.8 (d, *J* = 14.6 Hz, CH₂), 30.7 (d, *J* = 8.9 Hz, CH₂), 29.2 (d, *J* = 9.0 Hz, CH₂), 28.2 (d, *J* = 11.8 Hz, CH₂), 27.9 (d, *J* = 4.7 Hz, CH₂), 27.8 (s, CH₂), 27.5 (d, *J* = 8.0 Hz, CH₂), 26.6 (s, 2 x CH₂). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ (ppm) -12.3. **Crystal data for (±)-11b.** C₂₇H₄₀FeNOP, *M* = 481.42, *T* = 150 K; triclinic *P*-1 (I.T.#2), *a* = 8.1886(9), *b* = 11.7712(11), *c* = 13.0146(13) Å, *α*

= 91.501(4), *β* = 94.190(3), *γ* = 101.417(3) °, *V* = 1225.3(2) Å³. *Z* = 2, *d* = 1.305 g·cm⁻³, *μ* = 0.700 mm⁻¹. A final refinement on *F*² with 5543 unique intensities and 280 parameters converged at ω*R*(*F*²) = 0.1025 (*R*(*F*) = 0.0406) for 4968 observed reflections with *I* > 2σ(*I*). CCDC 2090462.

1-Diphenylphosphino-1'-(*N*-morpholinomethyl)ferrocene (11c): By following the general procedure B from compound 8 (308 mg, 0.75 mmol, 1.00 equiv) and diphenylchlorophosphine (166 μL, 199 mg, 0.9 mmol), the crude product was obtained after column chromatography (PE/EtOAc, 60:40 to 40:60 with 2% of NEt₃). This was dissolved in THF (9 mL) at rt and BH₃-THF complex (1M in THF, 4.5 mL, 4.5 mmol, 6.00 equiv) was added and the reaction mixture was stirred at rt for 2 h. Water was added to the reaction mixture which was extracted with EtOAc. The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography, using PE-EtOAc (90:10 to 70:30) to give the phosphine-borane adduct (125 mg). This was dissolved in diethylamine (7.30 mL) at rt and the reaction mixture was stirred for 16 h. Volatiles were removed under vacuum to give the crude product. This was purified by column chromatography, eluting with PE-EtOAc (73:30 to 50:50, with 1% NEt₃) to give the title product as a yellow solid after trituration in pentane (2 mL) (72 mg, 21% over three steps). *R*_f (eluent: PE/EtOAc 70:30, 5 drops of NEt₃) = 0.43. Mp 119-120 °C. *v*_{max} (film)/cm⁻¹ 2965, 2924, 2859, 2805, 1478, 1452, 1433, 1329, 1287, 1270, 1116, 1071, 1027, 1005, 909, 866, 825, 811, 745. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.38-7.35 (m, 4H, ArCH, 4 x H^{2''}), 7.31-7.30 (m, 6H, ArCH, 4 x H^{3''} and 2 x H^{4''}), 4.33 (t, *J* = 1.5 Hz, 2H, FcCH, H3 and H4), 4.10 (t, *J* = 1.4 Hz, 2H, FcCH, H2' and H5'), 4.05 (q, *J* = 1.5 Hz, 2H, FcCH, H2 and H5), 4.03 (t, *J* = 1.4 Hz, 2H, FcCH, H3' and H4'), 3.64 (t, *J* = 4.5 Hz, 4H, 2 x CH₂O), 3.07 (s, 2H, CH₂), 2.32 (s, 4H, 2 x CH₂N). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 139.3 (d, *J* = 9.7 Hz, ArC, 2 x C^{1''}), 133.4 (d, *J* = 19.6 Hz, ArCH, 4 x C^{2''}), 128.7 (s, ArCH, 2 x C^{4''}), 128.3 (d, *J* = 6.8 Hz, ArCH, 4 x C^{3''}), 8.1 (s, FcC, C^{1''}), 76.3 (d, *J* = 6.4 Hz, FcC, C1), 73.6 (d, *J* = 14.9 Hz, FcCH, C2 and C5), 71.6 (d, *J* = 2.5 Hz, FcCH, C3 and C4), 71.5 (s, FcCH, C2' and C5'), 69.5 (s, FcCH, C3' and C4'), 66.9 (s, 2 x CH₂O), 58.3 (s, CH₂), 53.2 (s, 2 x CH₂N). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ (ppm) -16.9.

(±)-1-Dicyclohexylphosphino-2-(*N*-morpholinomethyl)ferrocene palladium dichloride complex ((±)-12): Compound (±)-11b (48.1 mg, 1.00 mmol, 1.00 equiv) and PdCl₂.MeCN₂ (25.9 mg, 1.00 mmol, 1.00 equiv) were charged in a Schlenk tube which was subjected to three cycles of vacuum/argon. Anhydrous CH₂Cl₂ (1 mL) was added and the reaction mixture was stirred at 30 °C for 16 h. Volatiles were removed under vacuum and the resulting solids were triturated with pentane (2 x 2 mL) to afford the title product (±)-12 as a red solid (55.1 mg, 84%). Mp 130-131 °C (decomp). *v*_{max} (film)/cm⁻¹ 2923, 2851, 1446, 1248, 1214, 1163, 1110, 1003, 909, 849, 820, 725. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.56 (dt, *J* = 3.7, 12.9 Hz, 1H), 4.65 (s, 1H), 4.60 (s, 1H), 4.57 (s, 1H), 4.36 (s, 5H, Cp), 4.22 (dd, *J* = 6.1, 13.3 Hz, 1H), 4.09 (t, *J* = 12.1 Hz, 1H), 3.95 (dt, *J* = 2.6, 13.2 Hz, 1H), 3.85 (d, *J* = 13.2 Hz, 1H), 3.72-3.67 (m, 2H), 3.40 (d, *J* = 11.8 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 2.69-2.62 (m, 1H), 2.45-2.43 (m, 1H), 2.36-2.32 (m, 1H), 2.28 (d, *J* = 13.2 Hz, 1H), 2.22-2.19 (m, 1H), 2.09-2.05 (m, 3H), 1.98-1.96 (m, 2H), 1.89-1.75 (m, 4H), 1.67-1.65 (m, 1H), 1.45-1.39 (m, 4H), 1.27-1.16 (m, 4H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ (ppm) 28.2. HRMS (ESI⁻) *m/z*: [M+Cl]⁻ Calcd for C₂₇H₄₀NO³⁵Cl₃P⁵⁶Fe¹⁰⁶Pd 692.03028; Found 692.0304. HRMS (ESI⁺) *m/z*: [M-Cl]⁺ Calcd for C₂₇H₄₀NO³⁵ClP⁵⁶Fe¹⁰⁶Pd 622.09147; Found 622.0915.

4-(4-Methoxyphenyl)acetophenone (15): 4-Methoxyphenylboronic acid (114 mg, 0.75 mmol, 1.50 equiv), Pd(OAc)₂ (2.24 mg, 0.010 mmol, 0.020 equiv), ligand (±)-11b (9.63 mg, 0.020 mmol, 0.040 equiv) and CsF (228 mg, 1.50 mmol, 3.00 equiv) were charged in a Schlenk tube which was subjected to three cycles of vacuum/argon. 4-Chloroacetophenone (65.0 μL, 77.3 mg, 0.50 mmol, 1.00 equiv) and dioxane (2.5 mL) were added and the reaction mixture was heated at 100 °C overnight (oil bath, external temperature). The reaction mixture was cooled to rt, water (4 mL) and EtOAc (2 mL) were added and the layers were separated. The aqueous

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layer was extracted with EtOAc (2 x 2 mL), the combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE/EtOAc (90:10) to give the title product as a white solid (109 mg, 96%). Analytical data analogous to those reported previously.^[54] R_f (eluent: PE/EtOAc 10:1) = 0.21. Mp 156–158 °C. ν_{\max} (film)/cm⁻¹ 2958, 2841, 1673, 1597, 1578, 1527, 1495, 1400, 1359, 1291, 1269, 1252, 1197, 1184, 1031, 1010, 998, 957, 814. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.01 (d, J = 8.4 Hz, 2H, 2 x ArCH), 7.65 (d, J = 8.4 Hz, 2H, 2 x ArCH), 7.58 (d, J = 8.7 Hz, 2H, 2 x ArCH), 7.00 (d, J = 8.7 Hz, 2H, 2 x ArCH), 3.87 (s, 3H, CH₃O), 2.63 (s, 3H, CH₃). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ (ppm) 197.8 (C=O), 160.1 (ArCO), 145.5 (ArC), 135.5 (ArC-CO), 132.4 (ArC), 129.1 (2 x ArCH), 128.6 (2 x ArCH), 126.8 (2 x ArCH), 114.6 (2 x ArCH), 55.5 (CH₃O), 26.8 (CH₃). Mass: 226 [M], 211 [M-CH₃].

4-Morpholinobenzonitrile (17): 4-Chlorobenzonitrile (68.8 mg, 0.50 mmol, 1.00 equiv), Pd(dba)₂ (5.75 mg, 0.010 mmol, 0.020 equiv), ligand (**±**)-**11b** (9.60 mg, 0.020 mmol, 0.040 equiv) and tBuOK (78.5 mg, 0.70 mmol, 1.40 equiv) were charged in a Schlenk tube which was subjected to three cycles of vacuum/argon. Morpholine (52.5 μ L, 52.3 mg, 0.60 mmol, 1.20 equiv) and toluene (1.0 mL) were added and the reaction mixture was heated at 100 °C overnight (oil bath, external temperature). The reaction mixture was cooled to rt, water (4 mL) and EtOAc (2 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 2 mL), the combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE/EtOAc (70:30, with 1% of NEt₃) to give the title product as a light yellow solid (43 mg, 45%). Analytical data analogous to those reported previously.^[55] R_f (eluent: PE/EtOAc 70:30) = 0.32. Mp 74–76 °C. ν_{\max} (film)/cm⁻¹ 2831, 2216, 1604, 1515, 1453, 1383, 1266, 1244, 1180, 1113, 927, 833, 815. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.51 (d, J = 9.0 Hz, 2H, 2 x ArCH), 6.86 (d, J = 9.0 Hz, 2H, 2 x ArCH), 3.84 (t, J = 5.0 Hz, 4H, 2 x CH₂N), 3.27 (t, J = 5.0 Hz, 4H, 2 x CH₂O). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ (ppm) 153.6 (ArCN), 133.6 (2 x ArCH), 120.0 (CN), 114.2 (2 x ArCH), 101.1 (ArCCN), 66.6 (2 x CH₂O), 47.4 (2 x CH₂N). Mass: 188 [M], 130, 102 [M-C₄H₈NO].

α -(4-Cyanophenyl)acetone (19): 4-Bromobenzonitrile (91.0 mg, 0.50 mmol, 1.00 equiv), [Pd(allyl)Cl]₂ (2.70 mg, 7.50 μ mol, 1.5 mol%), ligand (**±**)-**11b** (9.60 mg, 30.0 μ mol, 6.0 mol%) and Cs₂CO₃ (329 mg, 1.00 mmol, 2.00 equiv) were charged in a Schlenk tube which was subjected to three cycles of vacuum/argon. Acetone (367 μ L, 290 mg, 5.00 mmol, 10.0 equiv) and dioxane (1.00 mL) were added and the reaction mixture was heated at 90 °C overnight (oil bath, external temperature). The reaction mixture was cooled to rt, water (4 mL) and EtOAc (2 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 2 mL), the combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by preparative TLC over SiO₂, using PE/EtOAc (80:20 to 70:30) to give the title product as a white solid (39 mg, 49%). R_f (eluent: PE/EtOAc 80:20) = 0.18. Analytical data analogous to those reported previously.^[56] Mp 80–82 °C. ν_{\max} (film)/cm⁻¹ 3405, 3072, 2955, 2893, 2225, 1706, 1608, 1513, 1504, 1419, 1407, 1355, 1333, 1313, 1213, 1153, 1019, 979, 959, 911, 855, 789, 734. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.62 (d, J = 8.3 Hz, 2H, 2 x ArCH), 7.30 (d, J = 8.3 Hz, 2H, 2 x ArCH), 3.79 (s, 2H, CH₂), 2.21 (s, 3H, CH₃). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ (ppm) 204.4 (C=O), 139.5 (ArC), 132.5 (2 x ArCH), 130.5 (2 x ArCH), 118.8 (CN), 111.2 (ArC-CN), 50.5 (CH₂), 29.9 (CH₃). Mass: 159 [M], 117 [M-C₆H₄-CH₃].

CCDC deposition numbers. 2090455 (for **4a**), 2090456 (for **4n**), 1898629 (for **4r**), 2090457 (for **4u**), 2090458 (for **4v**), 2090459 (for **7a**), 1898630 (for **7b**), 2090460 (for **8a**), 2090461 (for **10**), 2090462 (for **11b**).

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